THIRD QUARTERLY REPORT

for

CHARACTERIZATION OF RECOMBINATION AND CONTROL
ELECTRODES FOR SPACECRAFT NICKEL-CADMIUM CELLS

December 9, 1966 - March 9, 1967

CONTRACT NO.: NAS 5-10241

Prepared By

GULTON INDUSTRIES, INC.
Alkaline Battery Division
212 Durham Ave.
Metuchen, N. J.

for

GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland

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CHARACTERIZATION OF RECOMBINATION AND CONTROL ELECTRODES FOR SPACECRAFT NICKEL-CADMIUM CELLS

by

S. Lerner and H. N. Seiger

ABSTRACT

Cells containing active Adhydrodes and fuel cell scavenger electrodes have been investigated as to their cycling and gassing characteristics at various temperatures. It has been shown that cells containing a fuel cell scavenger electrode have superior low temperature cycling, as well as gassing, characteristics when compared to standard VO-12HSAD cells.

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INTRODUCTION

High rate charging (rates in excess of C/5) of sealed nickel-cadmium batteries is a desirable mode of charge. Its desirability is due to the necessity of fast charging after deep discharge in low orbits, and also because a higher rate charge is efficient. High rate charging is avoided except where control of the amount of charge may be employed. When controlling, we must include some overcharge. The minimum input must be that which compensates for charge inefficiency, or else there will be a continual rundown in capacity, and the maximum input avoids building up pressures to the burst point. A good control stops or alters charge after the point where the overcharge compensates for charge inefficiency and before the point where the internal cell pressure becomes excessive, and avoids the wasteful heat produced when a cell goes into an overcharge mode.

A control that has many attractive attributes is the Adhydrode® (the adsorbed hydrogen electrode). By careful setting of the trip point, which is the signal across the load resistor between the Adhydrode and the negative electrode, a single level can safely and adequately control high rate charge over a suitable range of temperatures. The Adhydrode is, in a manner of speaking, a self-powered transducer. If the cell characteristics change with use or time, the result is that the signal generated will reflect this change. This situation does, in fact, occur. The negative electrodes recombine oxygen at decreasing rates over several hundred cycles. If we can get the oxygen recombination at faster rates, this disadvantage of the adhydrode can be overcome. An oxygen getter, or scavenger electrode, appears to be a reasonable approach to this problem.

The objective of this program is to produce cells containing the Adhydrode and scavenger electrodes. This will be accomplished through an investigation of materials as a scavenger electrode, and the fabrication of such cells and batteries for evaluation.

OUTLINE OF PROGRAM

The program has been completely outlined in the previous quarterly report and will be reviewed here only briefly. The program has been divided into three parts. The first involves the evaluation and improvement of scavenger electrodes. The second part of the program will be an evaluation of the third, or active Adhydrode, electrode characteristics. The final part of the program will be devoted to testing cells containing the best features determined from the first two parts of the program.

Testing of Scavenger Electrodes

Scavenger electrodes of the Adhydrode type, of various porosities and thicknesses, along with two different types of fuel cell electrodes, were tested to determine their ability to recombine oxygen. These were tested in both working cells and in a specially designed test chamber.[1]

Active (Third) Electrode

Three locations for the active electrode were studied; they are:

(1) A "U" shaped electrode placed in a side position.
(2) A flat plate electrode placed at one end of the pack.
(3) A flat plate electrode placed in the center of the pack.

Testing

When the optimum configurations for the scavenger and signaling electrodes have been determined, they will be used in combination for final testing.

Temperature Characteristics. - The above cells shall be tested at four different temperatures and three different depths of discharge.[1] The test shall be 1 week's cycling at each temperature and depth of discharge using a 60-30 minute orbit.

Life Testing. - The best cells will be life tested at room temperature at both 40% and 60% depths of discharge using a 60-30 minute orbit.

EXPERIMENTAL PROCEDURES & RESULTS

Automatic Cycling of Cells at Room Temperature

Several cells (Nos. 41, 42 and 43) with Adhydrodes and fuel cell electrode scavengers have been on various automatic cycling routines for the past six months at 60% depth of discharge. The first routine of 476 cycles consisted of a 60 minute charge followed by a 30 minute discharge. Cell number 42 was chosen as the control cell. The Adhydrode was connected to the negative through a 1/4 ohm resistor. Figures 1, 2, and 3 are the Adhydrode signal versus pressure curves for cycles 10, 228, and 461 for cell 42. At the end of the 476th cycle, the cells were placed on an instrument which allows the cells to be charged for 60 minutes or to a preset Adhydrode signal, and discharged for 30 minutes. If the Adhydrode signal point is reached before the end of 60 minutes, the cells are then automatically placed on open circuit for the remainder of the 60 minutes, and then go on the discharge portion of the cycle.

The cells were connected to the cycler using cell 42 as the control cell. A 1/4 ohm resistor was connected between the Adhydrode and the negative and the trip point was set at 50 mV (200 mA). This trip point setting allowed for a 10% overcharge. Figures 4 and 5 are the Adhydrode versus pressure curves for cycles 4 and 97 for the control cell.

After the 144th cycle, the cell voltages began to fall below 1.0 V at the end of discharge, due to a slight increase in the Adhydrode sensitivity, causing the cells to be taken off charge prematurely.

To overcome this, the 1/4 ohm resistor was replaced by a 1/8 ohm resistor and the trip point reset at 45 mV. This again allowed for a 10% overcharge. Figures 6 and 7 are the Adhydrode signal versus pressure for cycles 193 and 305. On the 326th cycle, the Adhydrode on the controlling cell ceased to function in a stable manner, and the cells began to receive a full 60 minutes of charge, which corresponds to a 32% overcharge. However, even with this extreme overcharge, the end of charge cell pressures remained below 25 psig.

In order to determine the cause of the erratic Adhydrode behavior, the cell atmosphere in the control cell was analyzed after the end of charge of the 367th cycle and found to contain 95% hydrogen. Comparison of control and experimental cells both show the presence of hydrogen, so this is not due to the scavenger electrode but may be due to the present batch of plates. However, the presence of hydrogen in the cells and the low end of charge pressure (12 psig), along with the fact that during discharge the cell returns to vacuum, illustrates the advantage of using a fuel cell electrode as a scavenger, since the build-up of extreme pressures is prevented regardless of the composition of the internal cell atmosphere. After the gas sample analysis, the cells were discharged to 1.0 V and were reconditioned. The reconditioning cycle consisted of a C/10 (800 mA) charge, a 3 ampere discharge to 1.0 V, a C rate charge, and a 3 ampere discharge to 1.0 V.

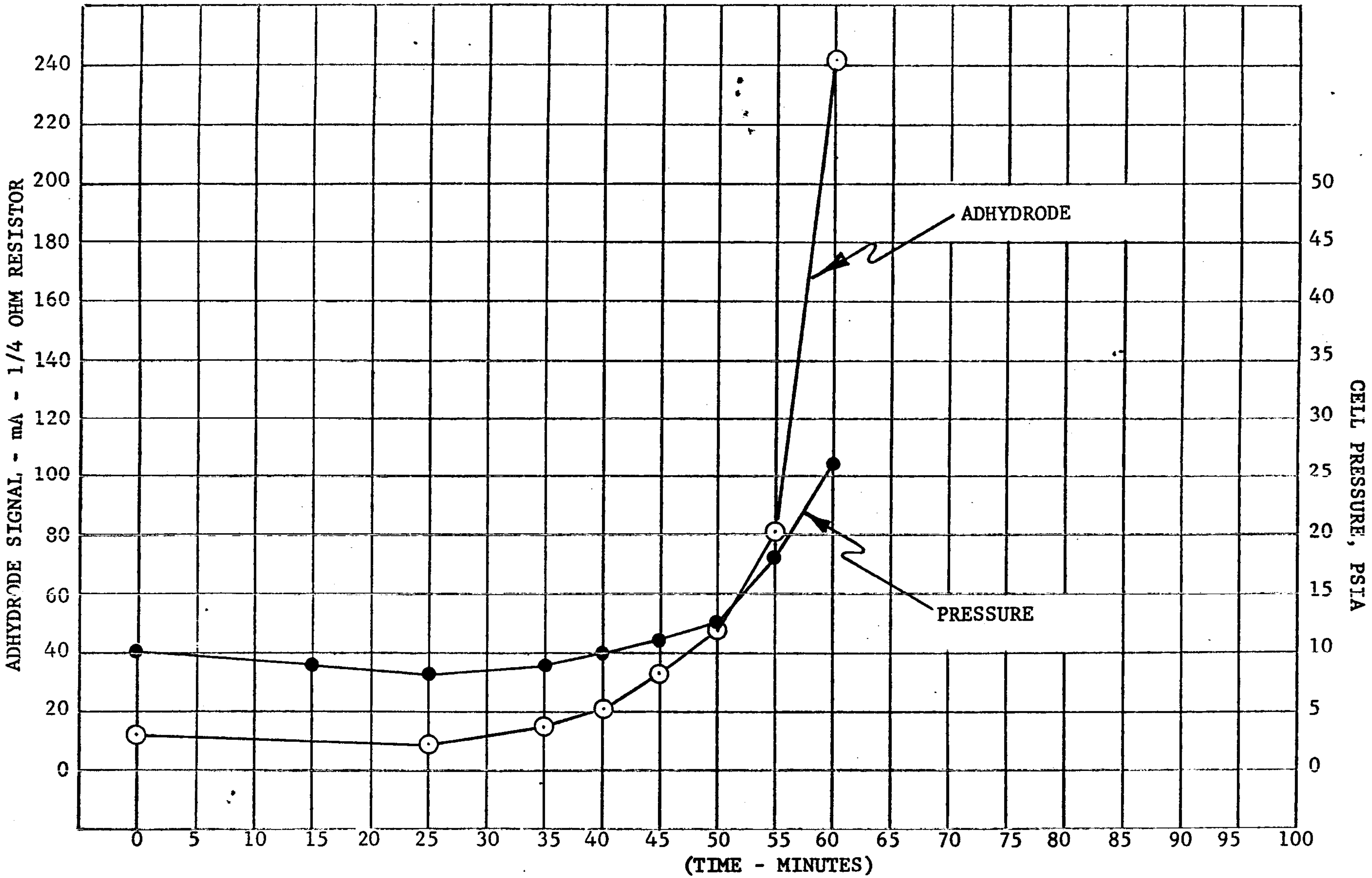

FIGURE 1. ADHYDRODE SIGNAL Vs PRESSURE, AUTOMATIC CYCLING, CELL NO. 42, CYCLE 10, 60% DOD
5.5 A charge - 10 A discharge

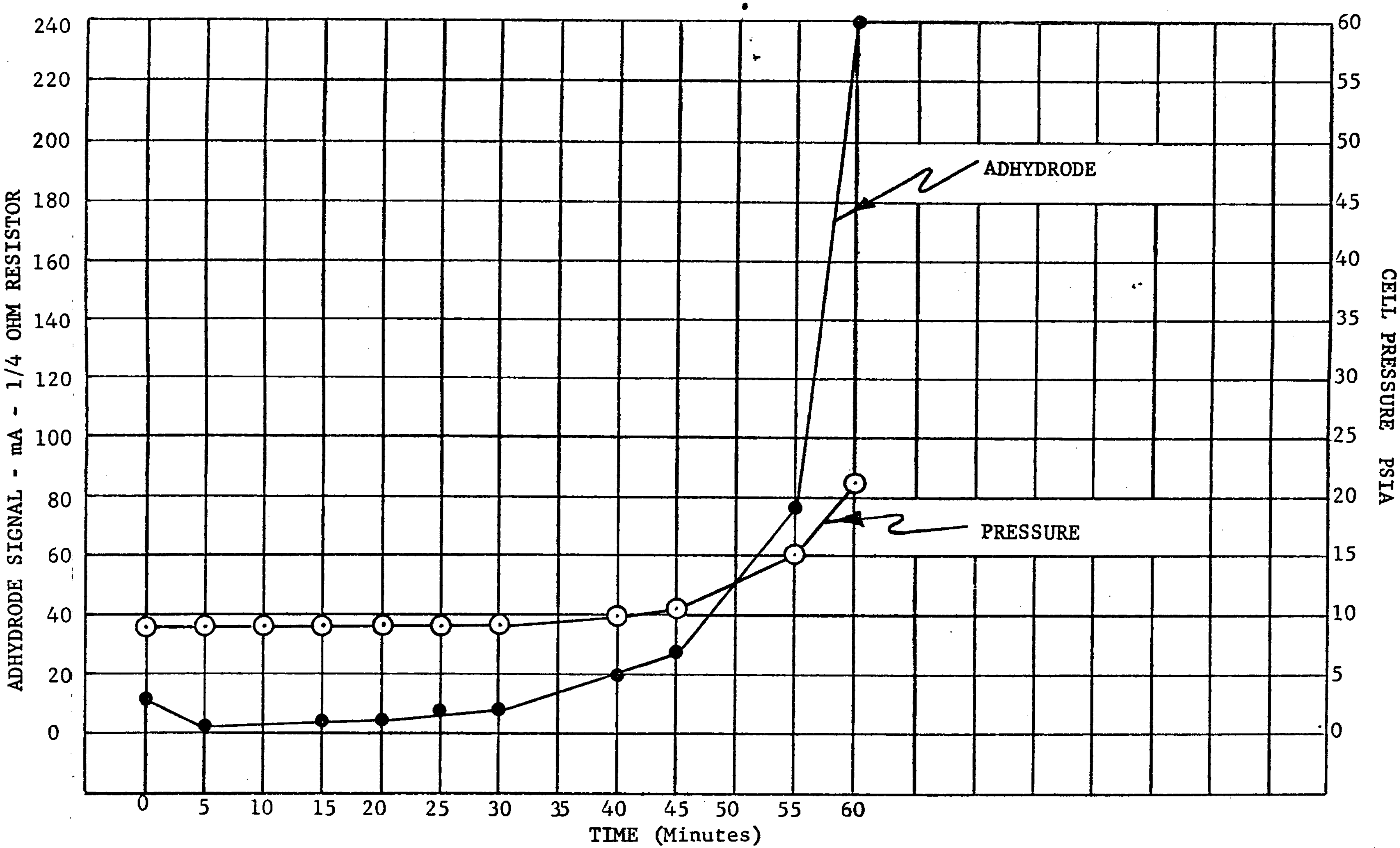

FIGURE 2 ADHYDRODE SIGNAL Vs. PRESSURE - AUTOMATIC CYCLING
CELL NO. 42, CYCLE 228, 60% DOD
5.5 A CHARGE - 10 A DISCHARGE

4-1190

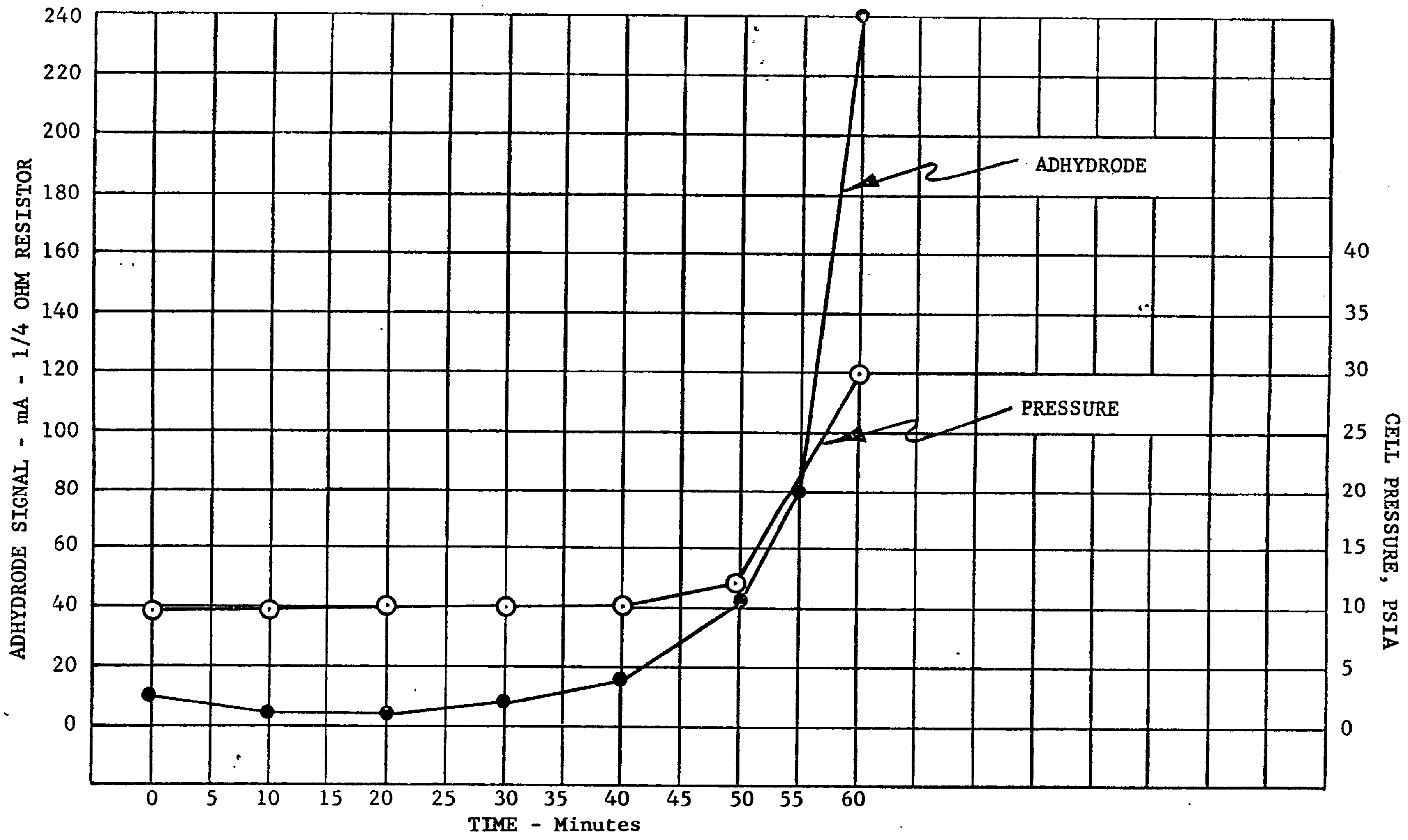

FIGURE 3 ADHYDRODE SIGNAL Vs. PRESSURE - AUTOMATIC CYCLING

CELL NO. 42, CYCLE 461, 60% DOD

5.5 A CHARGE - 10 A DISCHARGE

4-1192

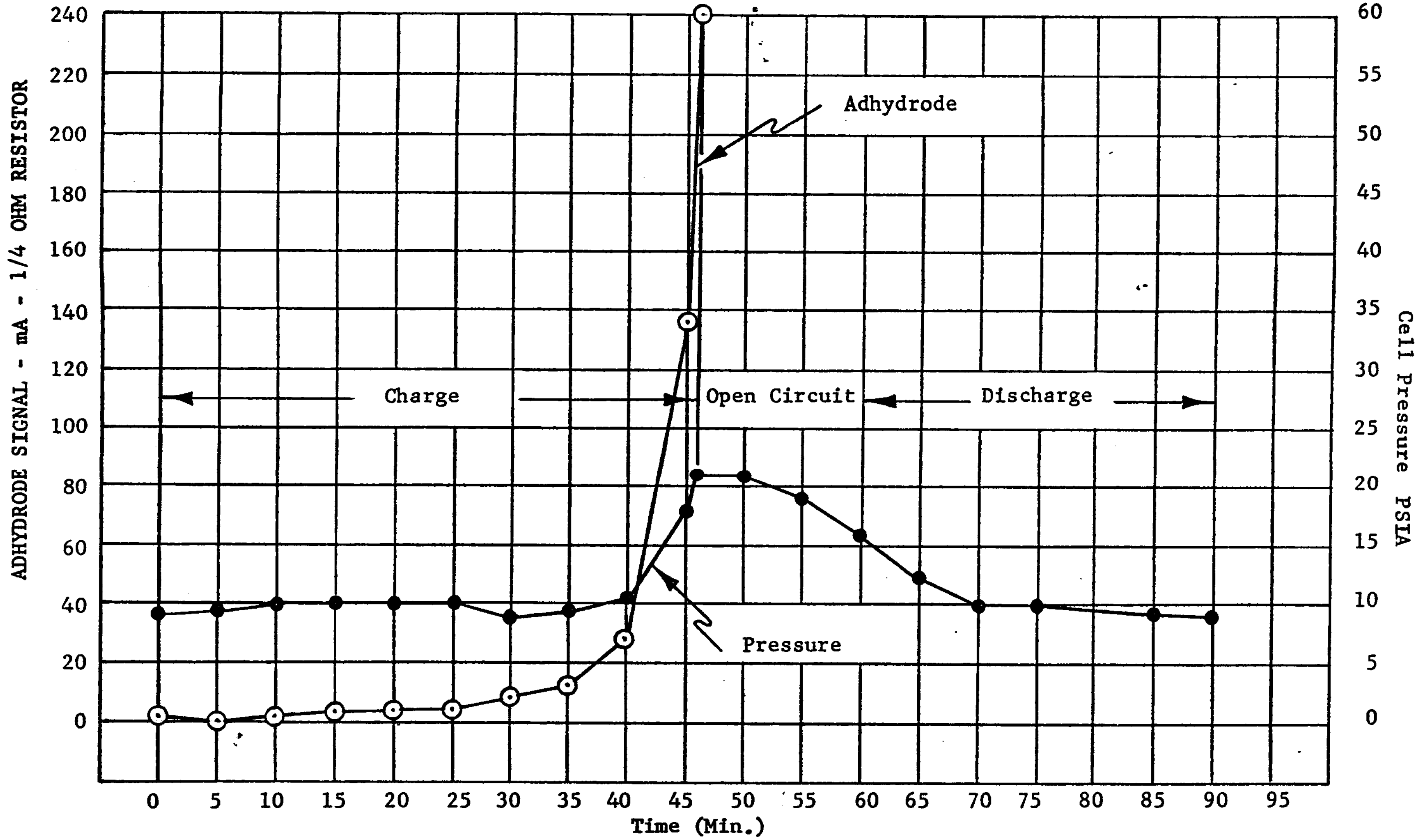

Figure 4 - Cell 42, 60% DOD, Cycle 4, Adhydrode Control
7A Charge, 9.5A Discharge

4-1210

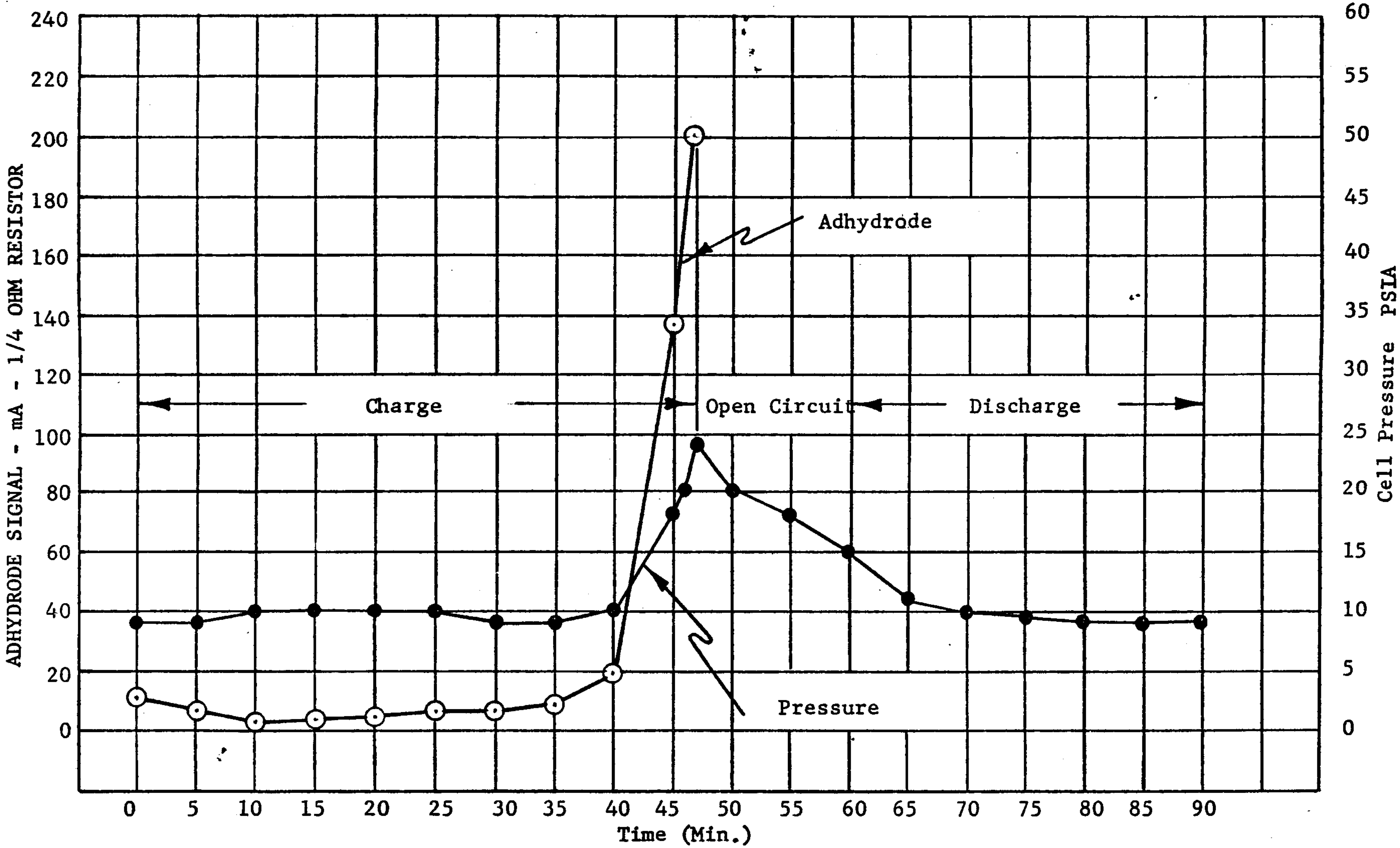

Figure 5 - Cell 42 60% DOD Cycle 97, Adhydrode Control
7A Charge - 9.5A Discharge

4-1211

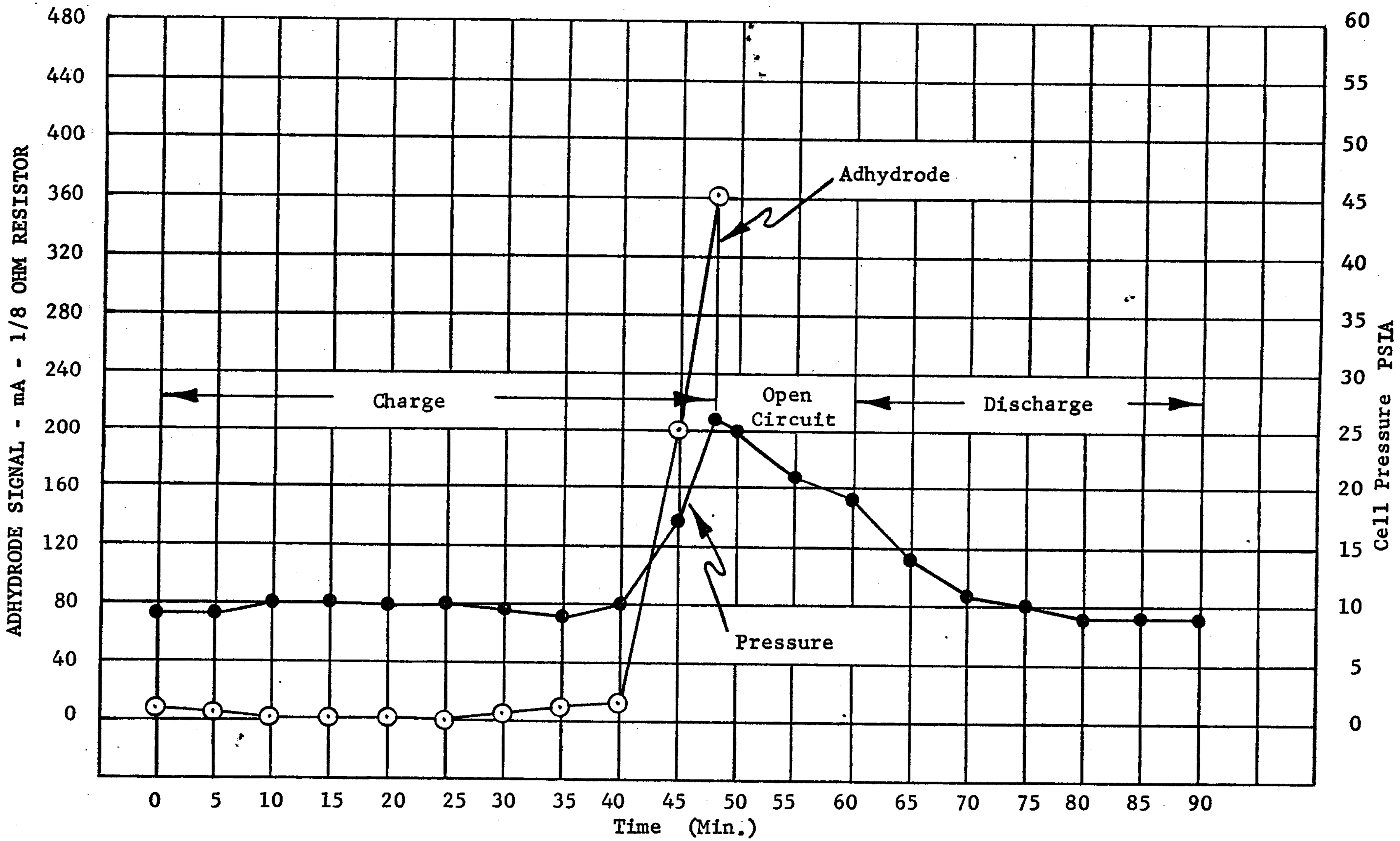

Figure 6 - Cell 42 60% DOD Cycle 193, Adhydrode Control
7A Charge - 9.5A Discharge

4-1212

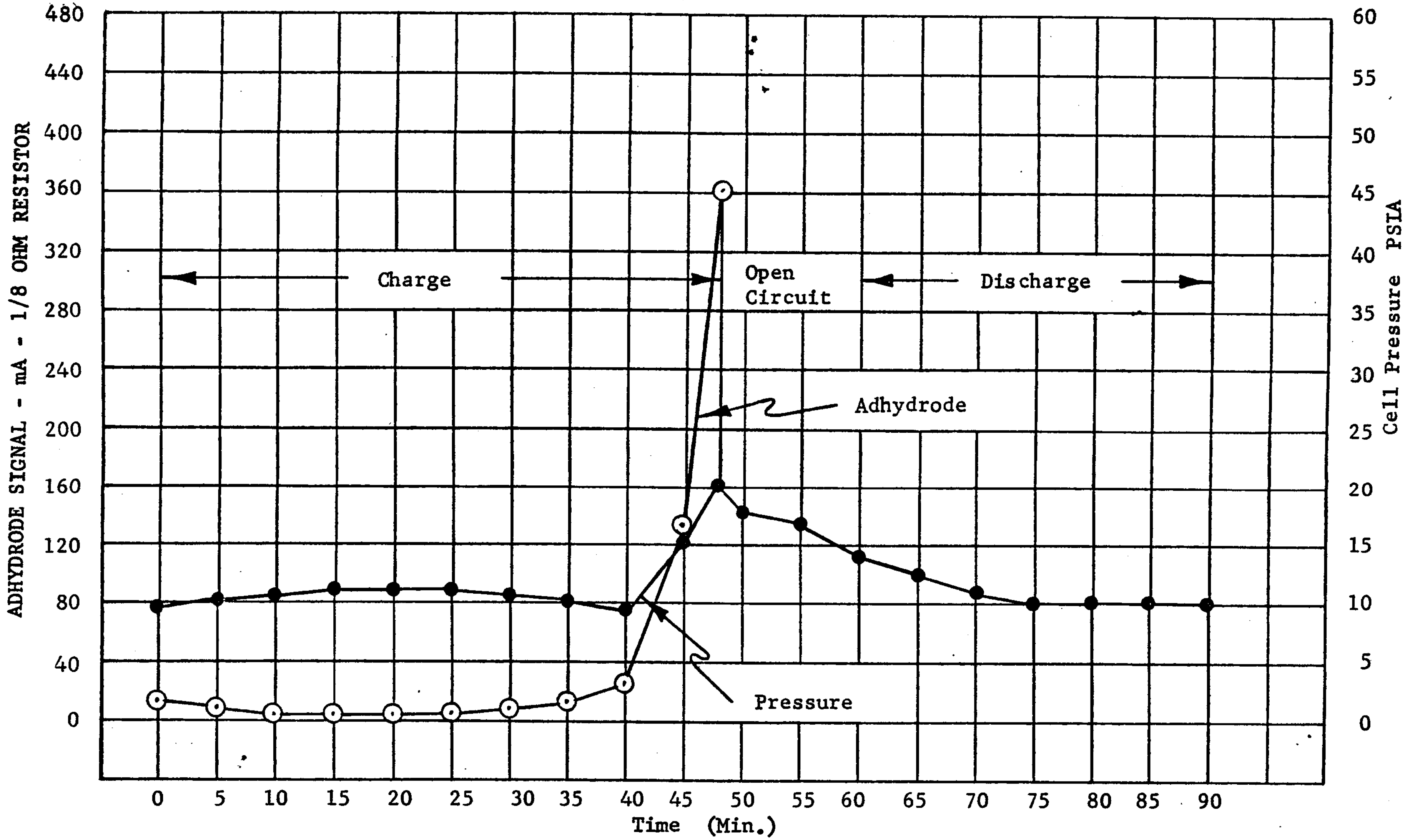

Figure 7 - Cell 42 60% DOD Cycle 305, Adhydrode Control
7A Charge - 9.5A Discharge

4-1213

Since prior to cycling, cell 42 had a capacity somewhat lower than the other cells, it is probable that part of the difficulties which arose during cycling were due to the severe loss in capacity of the control cell.

TABLE I. - CAPACITIES OF CELLS 41, 42, 43 UPON REMOVAL FROM CYCLING

CELL NO.	41	42	43
CAPACITY	7.8	5.1	7.7

After the reconditioning cycle, two of the cells (Nos. 40 and 43) were placed back on cycle with cell number 43 controlling and have, to date, successfully completed 398 cycles. Figures 8-10 are, respectively, cycles 61, 285, and 398. A comparison of these figures indicates that the recombination rate increases as the number of cycles increases. This may be due to a rise in the internal temperature of the cell which increases the rate of recombination; or a redistribution of electrolyte.

Low Temperature Cycling

Several control (VO-12HSAD) and experimental cells were cycled for one week at both -20°C (-4°F) and 0°C (32°F) at a 50% depth of discharge on a 90 minute orbit. Sixty-five cycles were completed at -20°C and sixty-one at 0°C. One complete cycle a day was monitored. Figures 11-14 are, respectively, the 3rd and last cycle for the experimental and control cells at -20°C. Figures 15-18 are similar curves at 0°C.

It should be noted that on the last cycle for the experimental cell at 0°C, the pressure begins to increase at the initiation of charge. The reason for this has not yet been investigated and no explanation is offered. However, this pressure rise is slight (10 psia) and apparently has no effect upon the cell characteristics which were a much more rapid pressure and Adhydrode decay than the control cells. In fact, the experimental cells had a stronger Adhydrode signal than the controls, which even at these low temperatures rose rapidly upon charge and decayed rapidly upon discharge, while the Adhydrode signal from the control cells rose, initially, on discharge and then decayed slowly. This rise and slow decay on discharge can be injurious to cycle life if the end of discharge signal is above the end of charge trip point as this can prevent some types of charge control devices from putting the cell back on charge.

On the last cycle at each temperature, the cells were discharged to 1.0 V and the residual capacities determined. These data are shown in Figures 19 and 20. It is evident that the experimental cells containing the fuel cell electrode have a greater resistance to capacity loss on low temperature cycling than the control cells. It should be noted that at low temperatures, the capacities of nickel-cadmium cells increases. However, the magnitude of this increase should be the same for both sets (control and experimental).

High Temperature Cycling

Three VO-12HSAD control cells and three experimental cells containing fuel cell scavenger electrodes were placed in an oven at 100°F in the discharged state. The cells were allowed to stand for 48 hours and were then charged at 5 amperes. During the initial charge, the control cells developed exceedingly high pressures (greater than 150 psig). Analysis indicated that the gas was $>$97% hydrogen. These cells, along with one experimental cell were removed from the oven and not tested further.

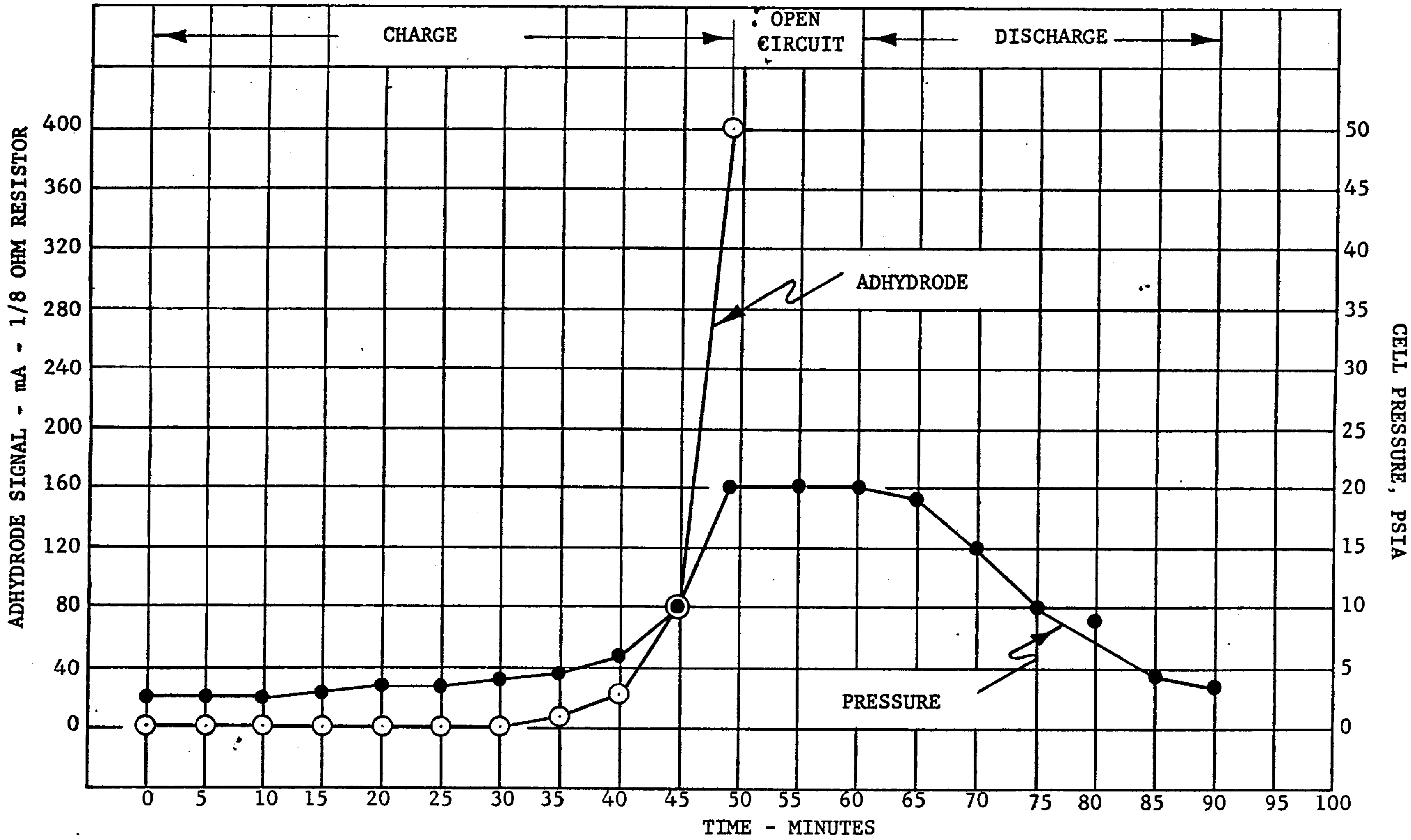

FIGURE 8. ADHYDRODE SIGNAL Vs. PRESSURE, CELL 43, CYCLE 61, 60% DOD, ADHYDRODE CONTROL
7A CHARGE - 9.5A DISCHARGE

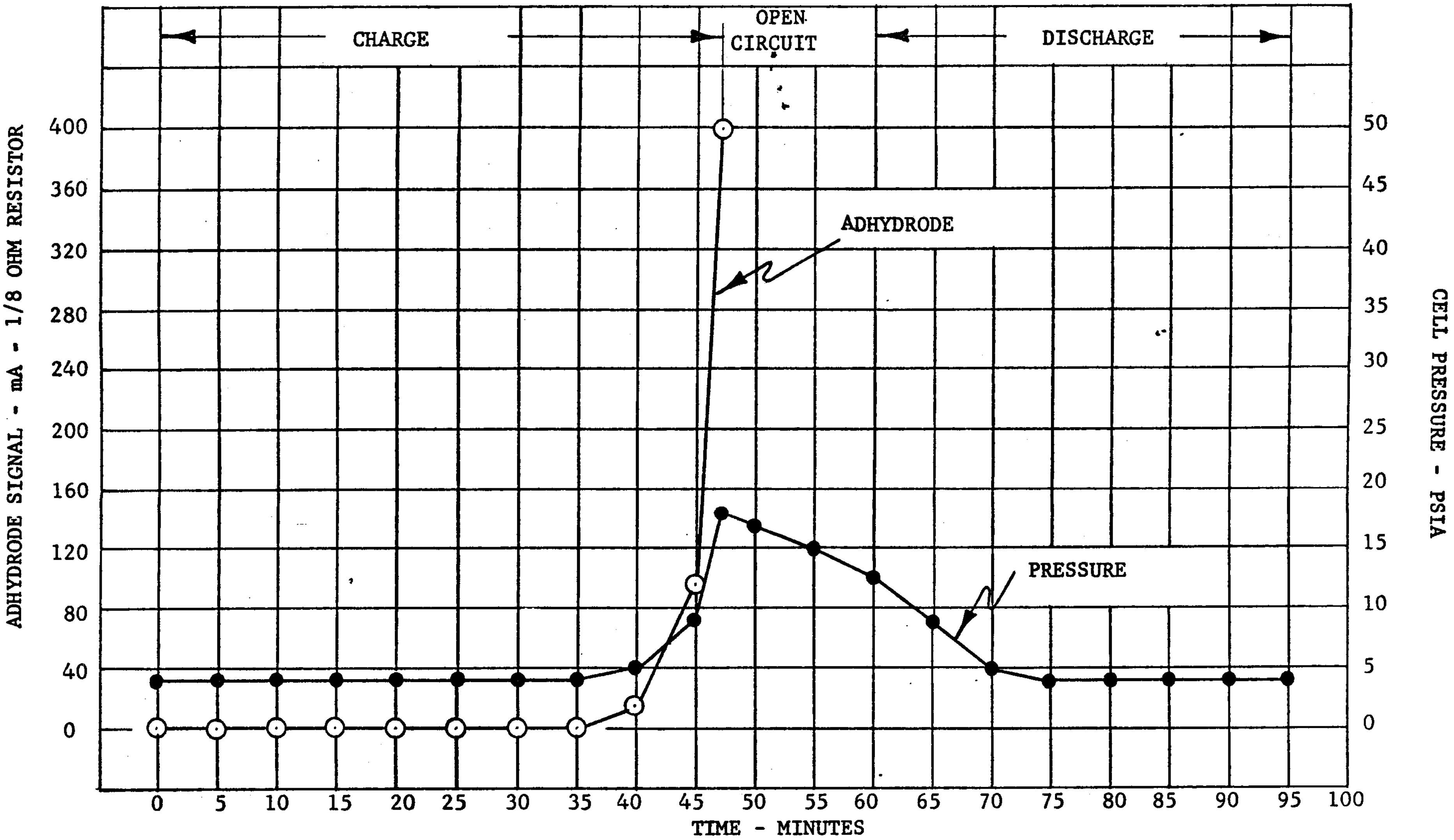

FIGURE 9. ADHYDRODE SIGNAL Vs. PRESSURE - CELL 43, CYCLE 285, 60% DOD, ADHYDRODE CONTROL
7A CHARGE - 9.5A DISCHARGE

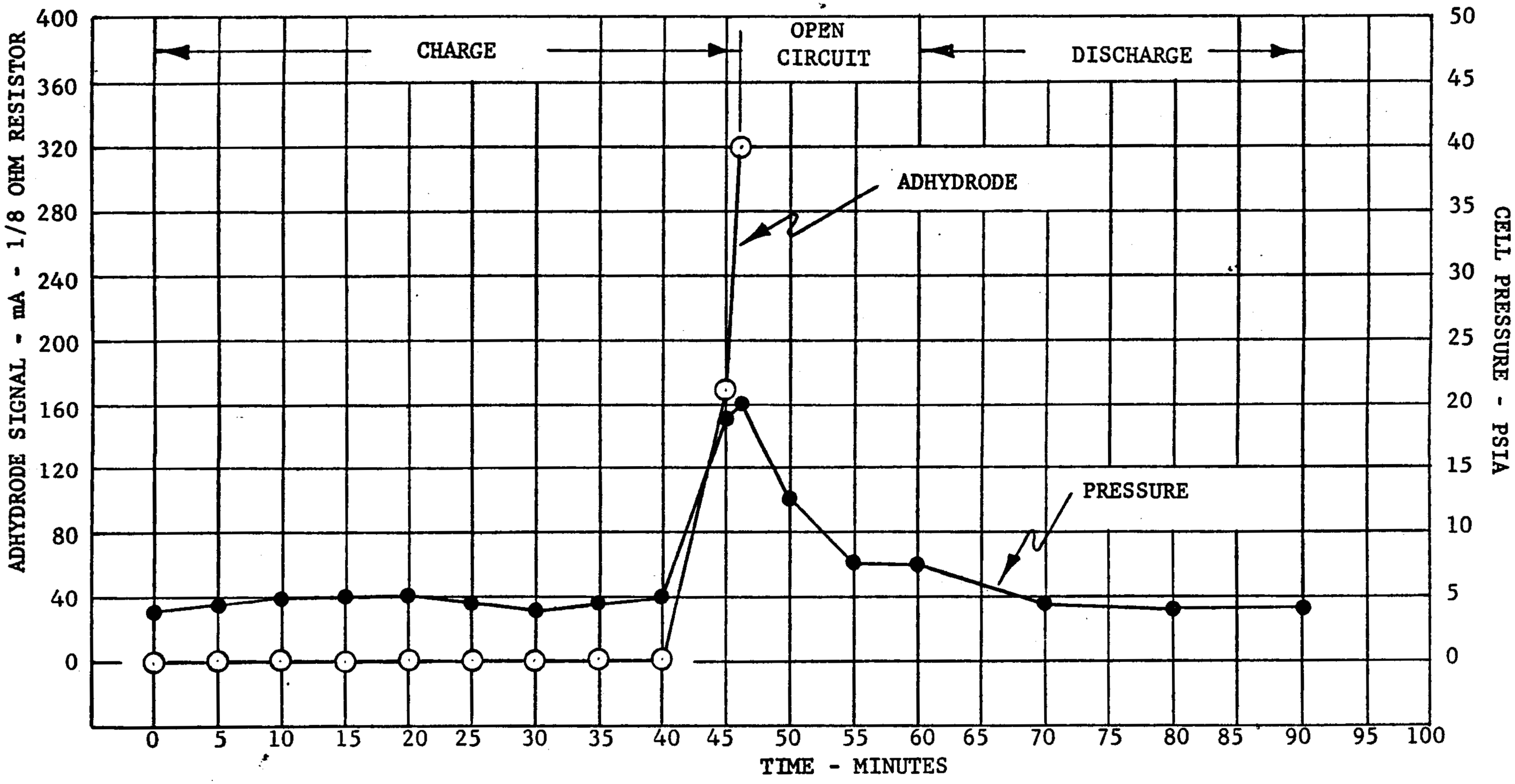

FIGURE 10. ADHYDRODE SIGNAL Vs PRESSURE, CELL 43, CYCLE 398, 60% DOD, ADHYDRODE CONTROL
7A CHARGE - 9.5A DISCHARGE

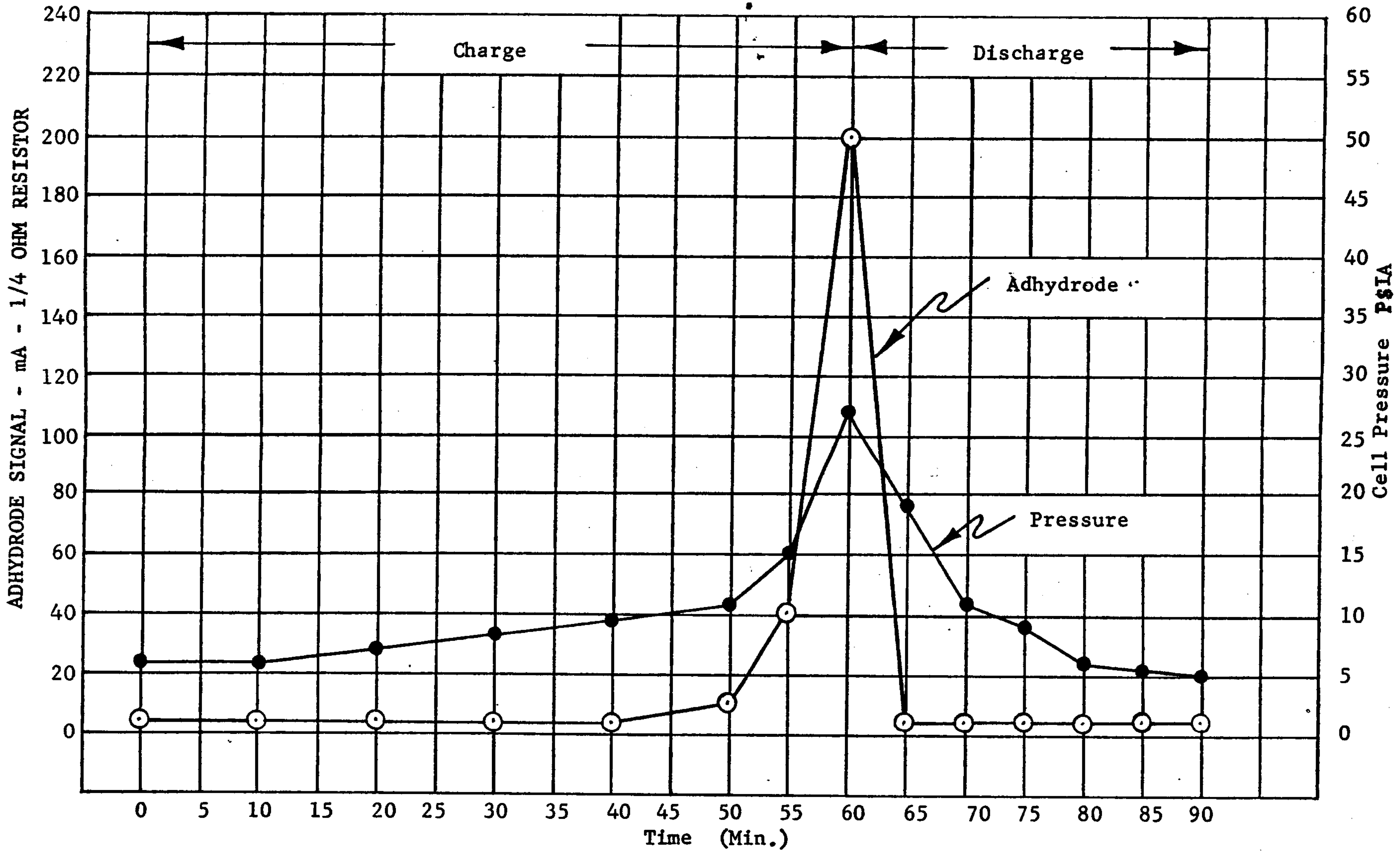

Figure 11 - Cycle 3 Exp. Cell 50% DOD -20°C (-4°F)

4-1214

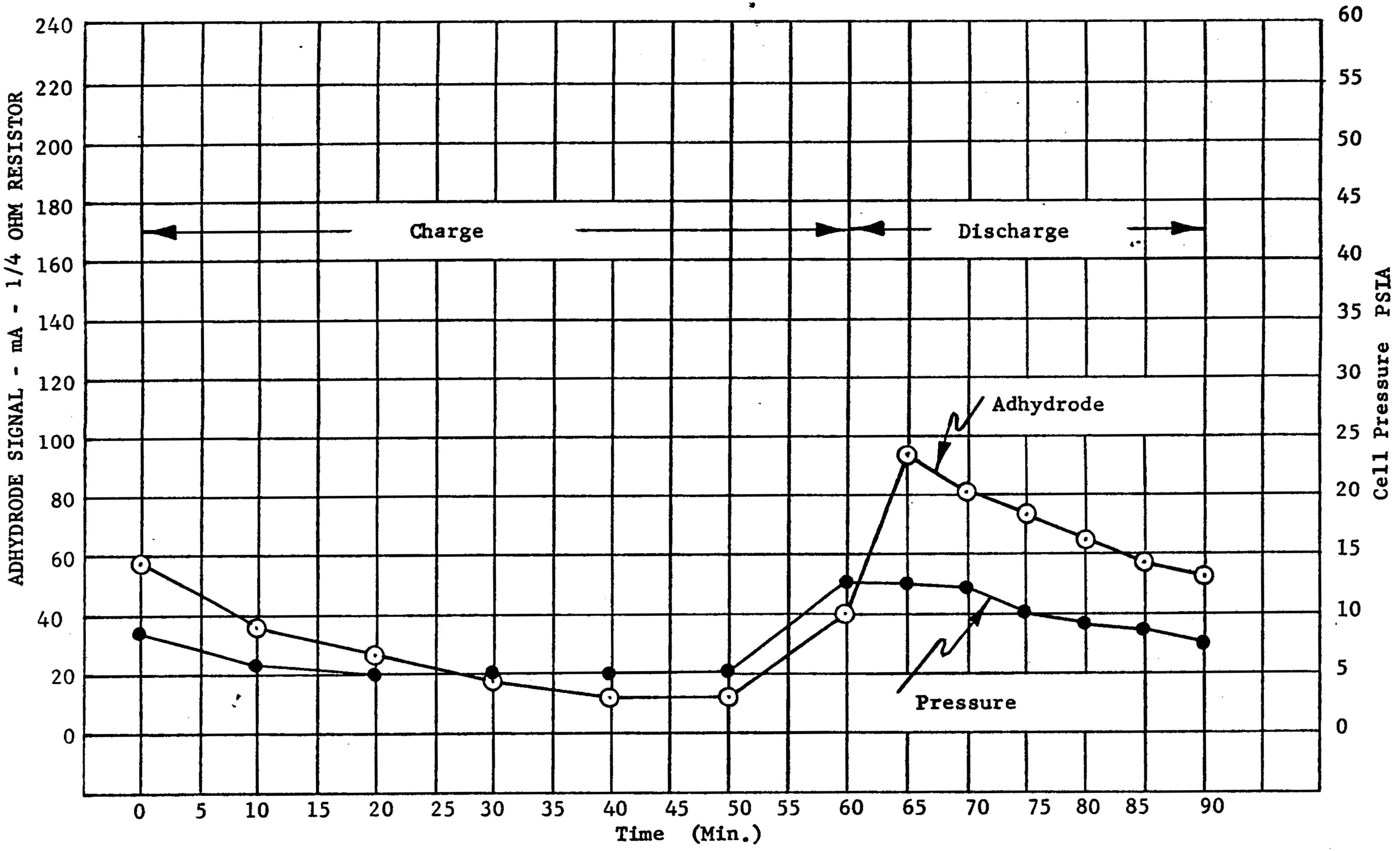

Figure 12- Cycle 3 Control Cell 50% DOD -20°C (-4°F)

4-1215

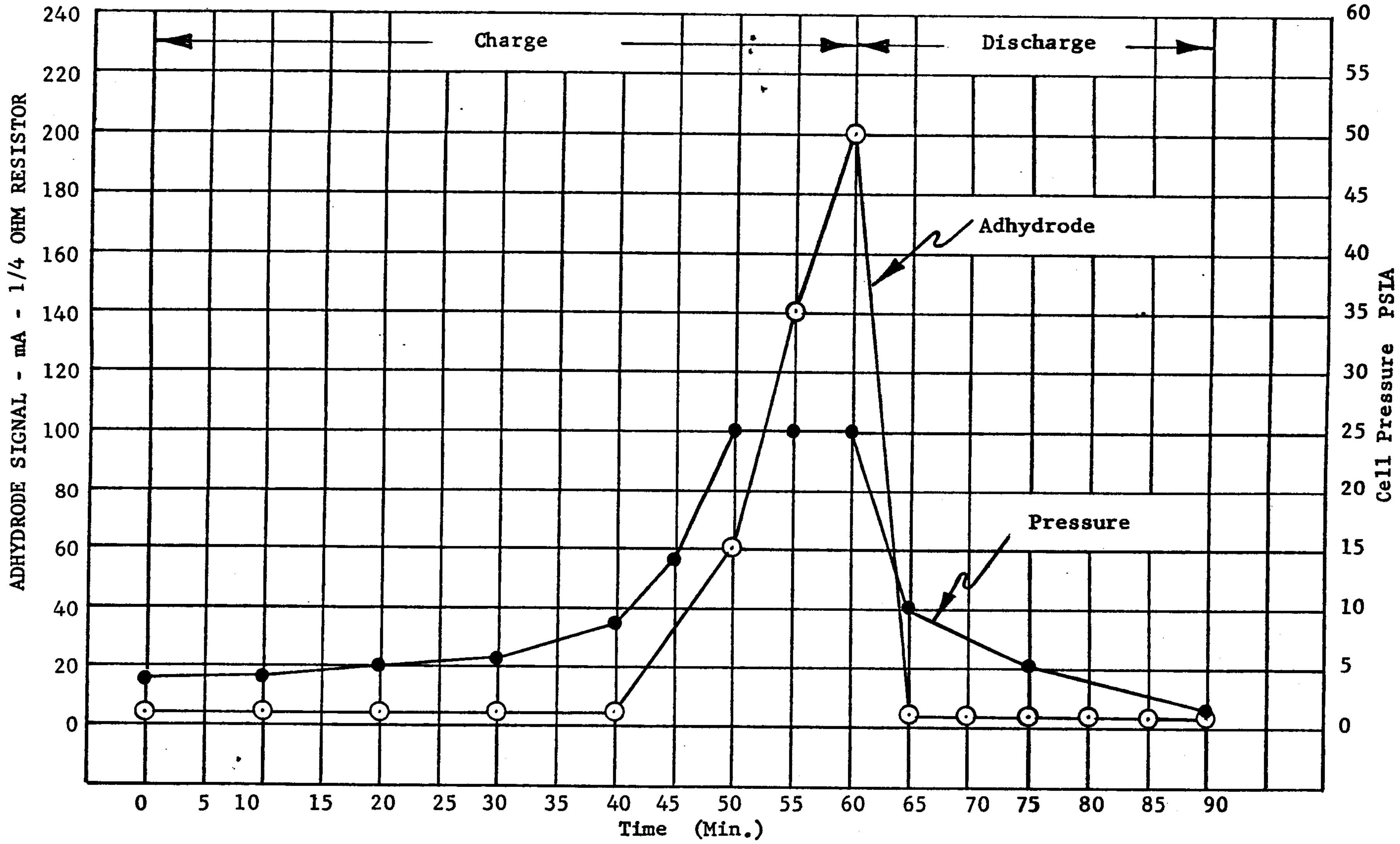

Figure 13 - Cycle 65 Exp. Cell 50% DOD -20°C (-4°F)

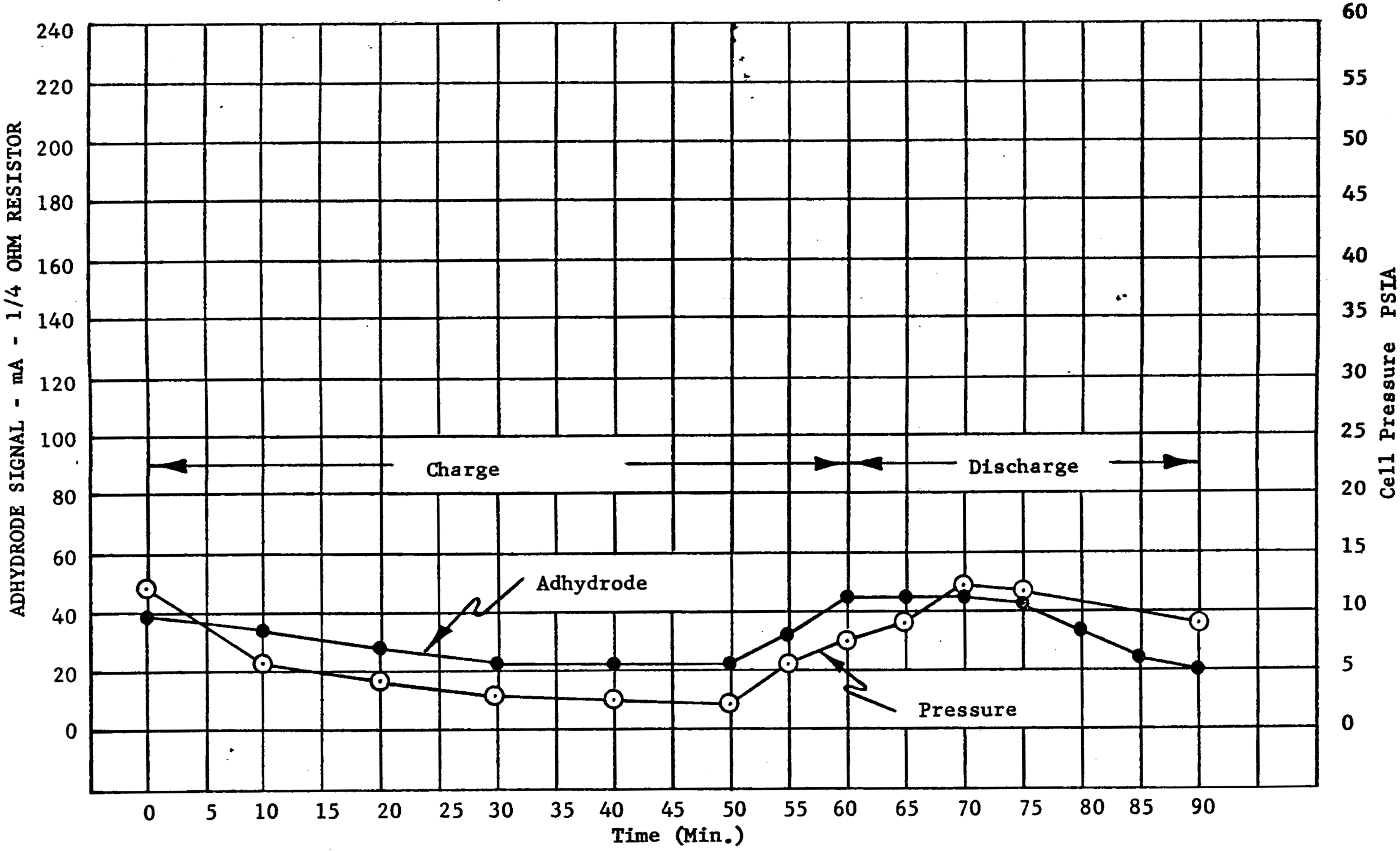

Figure 14- Cycle 65 Control Cell 50% DOD -20°C (-4°F)

4-1217

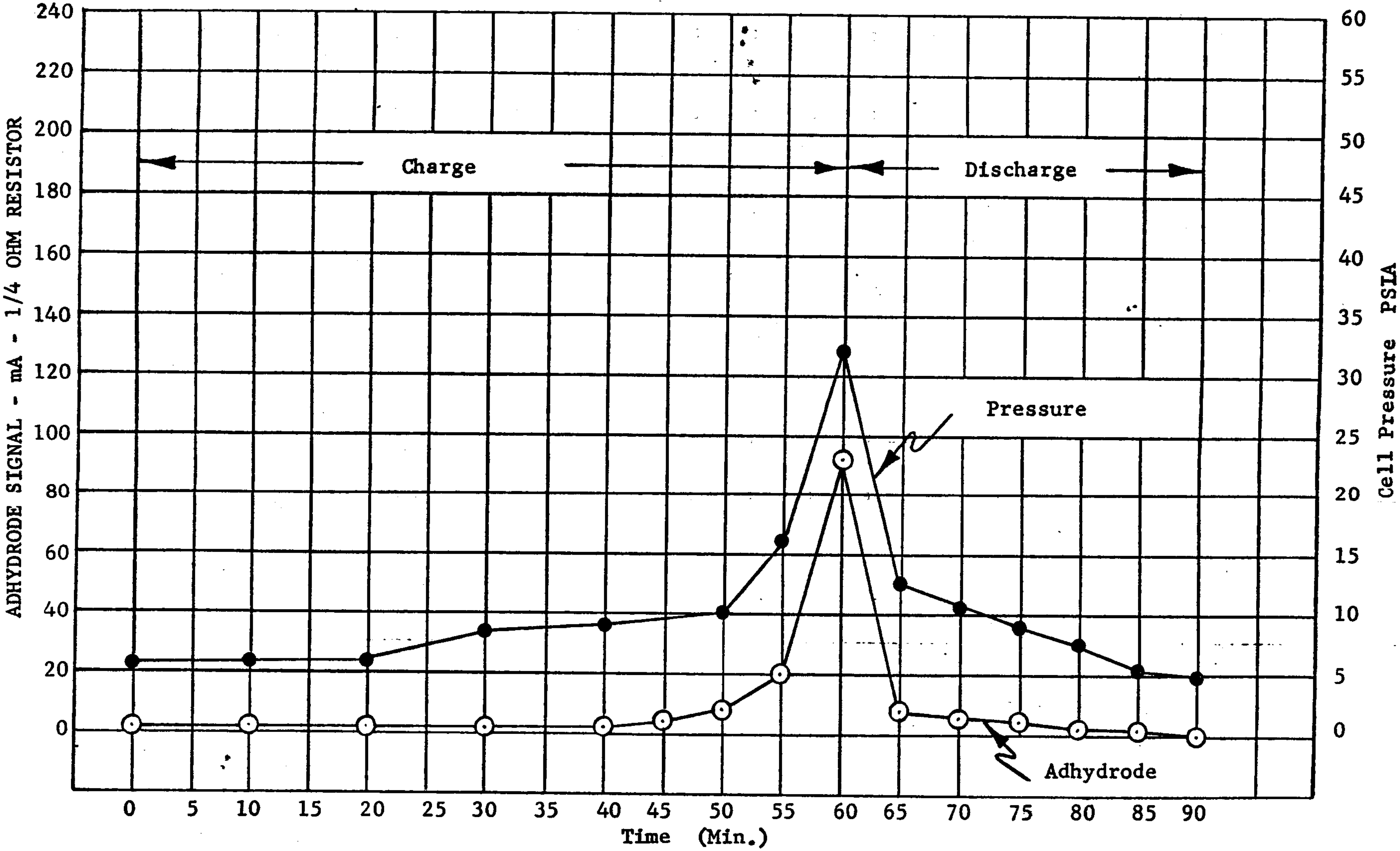

Figure 15- Cycle 3 Exp. Cell 50% DOD 0°C (32°F)

4-1218

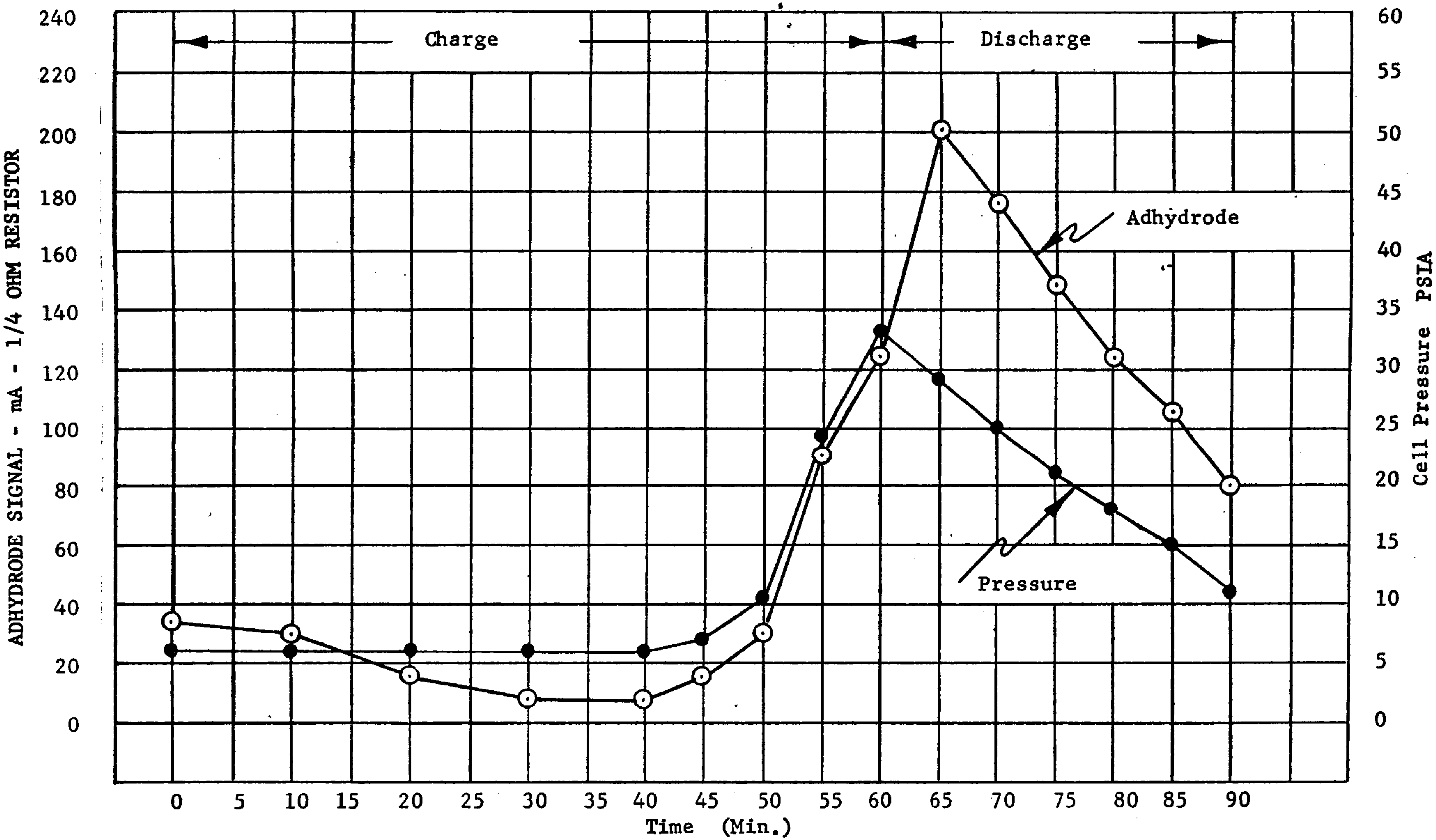

Figure 16 - Cycle 3 Control Cell 50% DOD 0°C (32°F)

4-1219

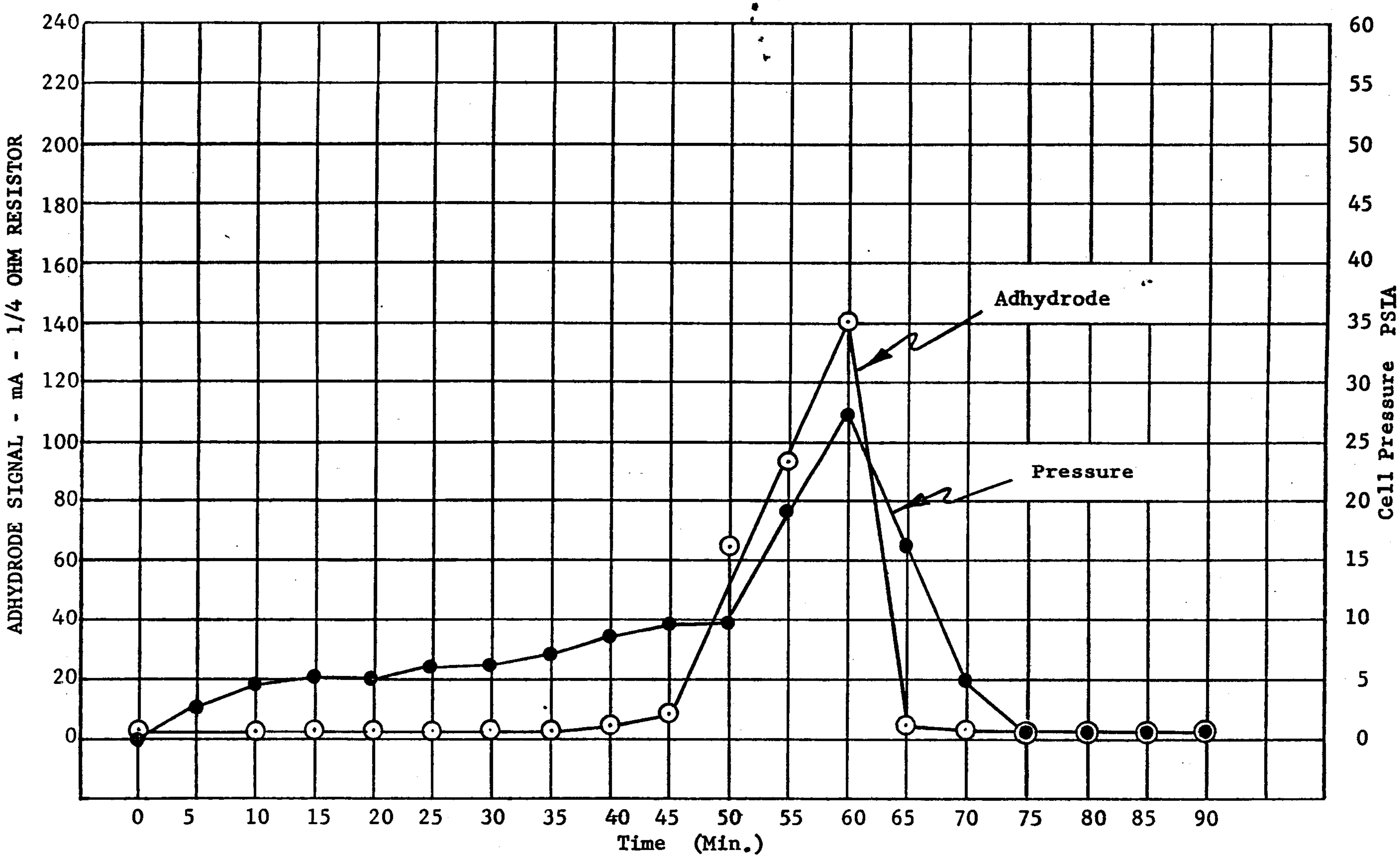

Figure 17 - Cycle 61 Exp. Cell 50% DOD 0°C (32°F)

4-1220

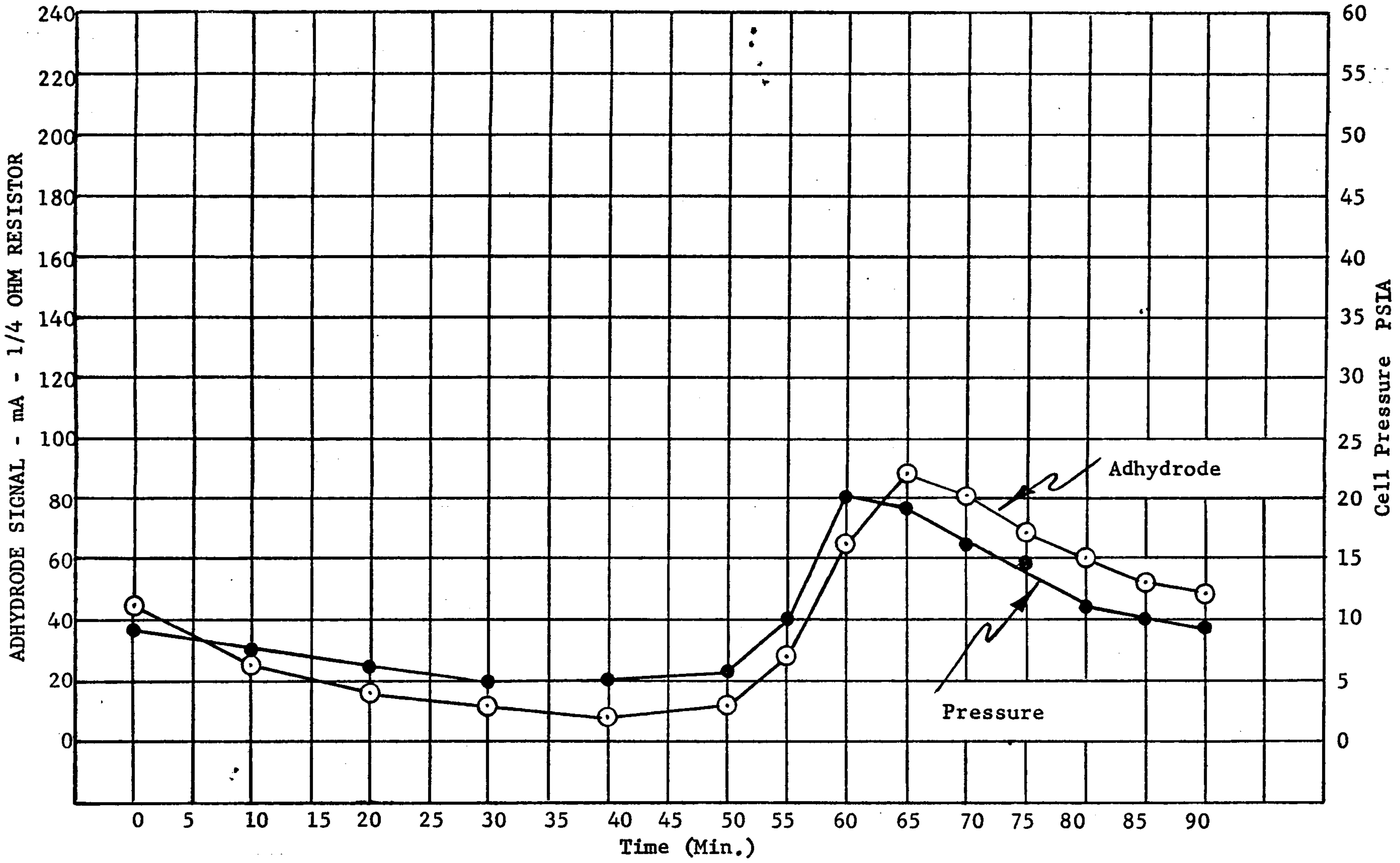

Figure 18 - Cycle 61 Control Cell 50% DOD 0°C (32°F)

4-1221

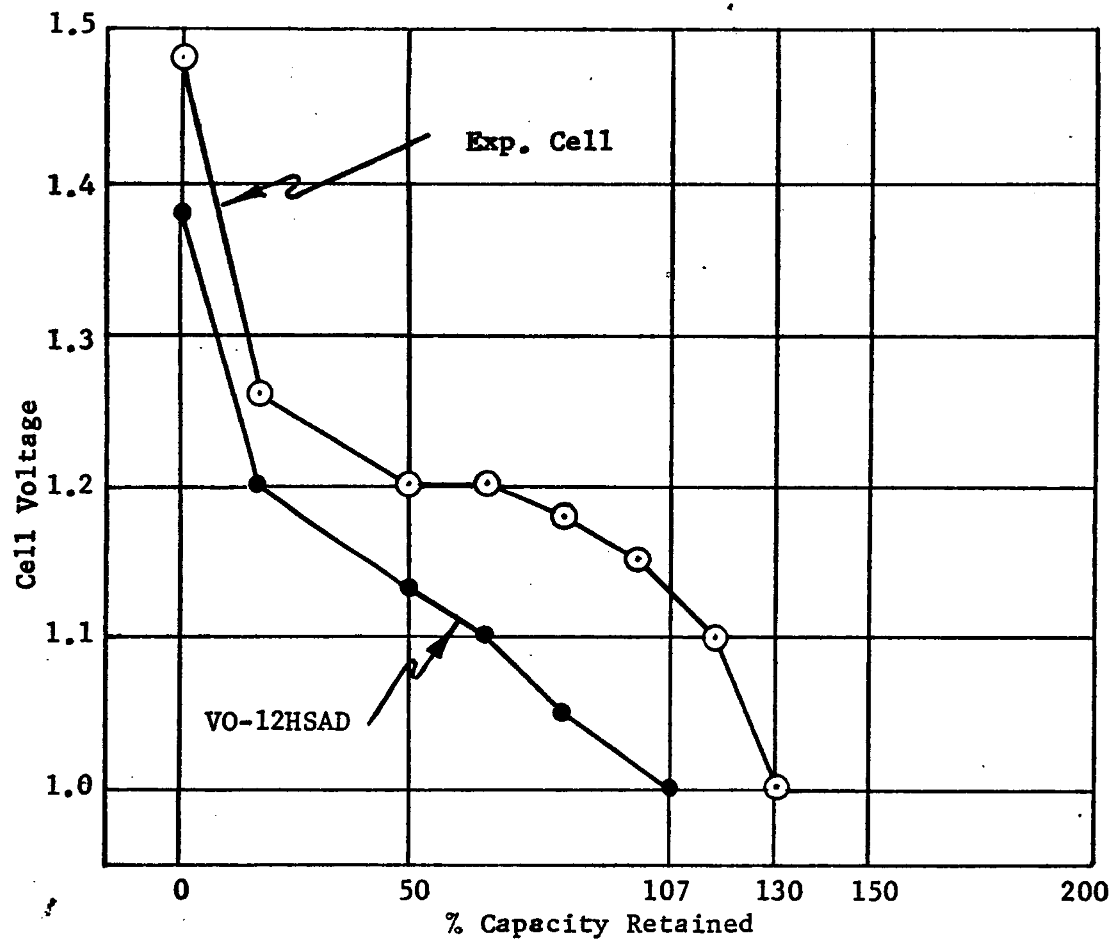

Figure 19 - Typical Residual Capacity After
65 → 50% DOD Cycles at -20°C (-4°F)

4-1222

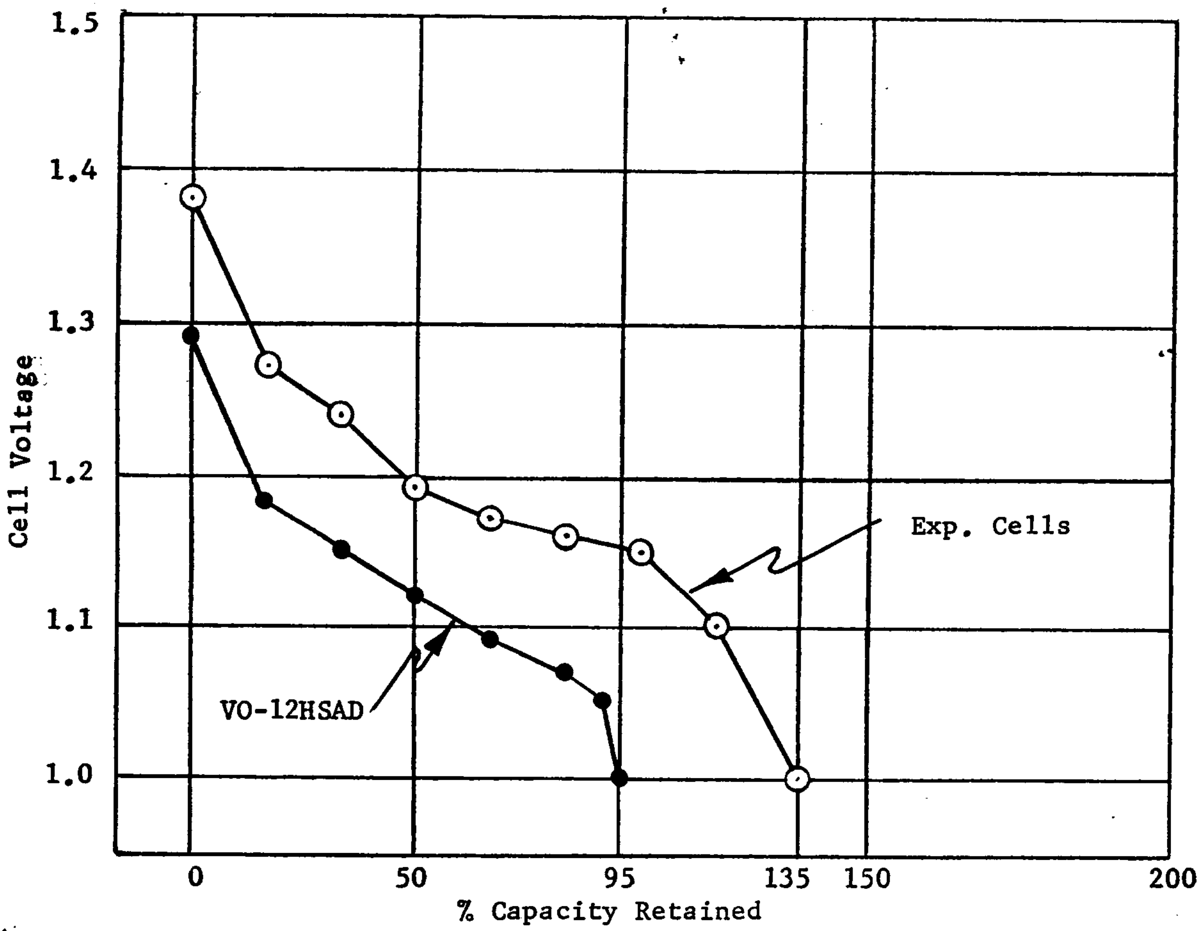

Figure 20 - Typical Residual Capacity After 61 - 50% DOD Cycles at $0^{o}C$ ($32^{o}F$)

4-1223

The remaining two experimental cells were placed on cycle at 50% depth of discharge. Both cells went into reverse on the first cycle. The two cells (discharged) were then allowed to equilibrate at 95°F. Eighteen cycles were completed before one cell went into reverse and the other cells' end of discharge voltage fell below 1.0 V (Figure 21).

To determine if the exposure to high temperatures had adversely affected the cells, the cells were placed on cycle at 50% depth of discharge for one week at room temperature. No problems were encountered during the room temperature cycling.

The cells were again placed in the oven at 100°F and were cycled at a 10% depth of discharge for 10 days (158 cycles). Figures 22 and 23 are the pressure, Adhydrode and discharge curve for cycles 3 and 142. Figure 24 is the residual capacity of the two cells after cycling (nominal cell capacity is 10 Ah).

Gassing Characteristics of Cells

In order to evaluate the gassing characteristics of the cells containing fuel cell electrodes, as compared to those cells containing a passive Adhydrode, the following test was performed.

Three cells containing fuel cell electrodes and three Vo-12HSAD cells (the Adhydrode in the passive mode) were charged at C/2 to 25 psig (40 psia) at temperatures between -20°C (0°F) and 40°C (100°F). The results for a typical pair of cells are shown in Figures 25 and 26 and briefly summarized in Table II. It is evident from these results that the inclusion of a fuel cell electrode in a sealed cell permits wider latitude in the charging mode and also aids in keeping the cell pressure at a low value.

The data presented for the VO-12HSAD cells are better than they would be under normal operating conditions, since under such conditions the Adhydrode would be connected in the active mode. This again shows the advantages to cells containing both scavenger and signaling electrodes.

TABLE II. - PERCENT CAPACITY INPUT TO 40 PSIA AT C/2 VERSUS TEMPERATURE

TEMPERATURE	VO-12HSAD	EXPERIMENTAL CELLS
-20°C (0°F)	108%	142%
0°C (32°F)	138%	158%
25°C (72°F)	79%	150%
40°C (100°F)	100%	150%

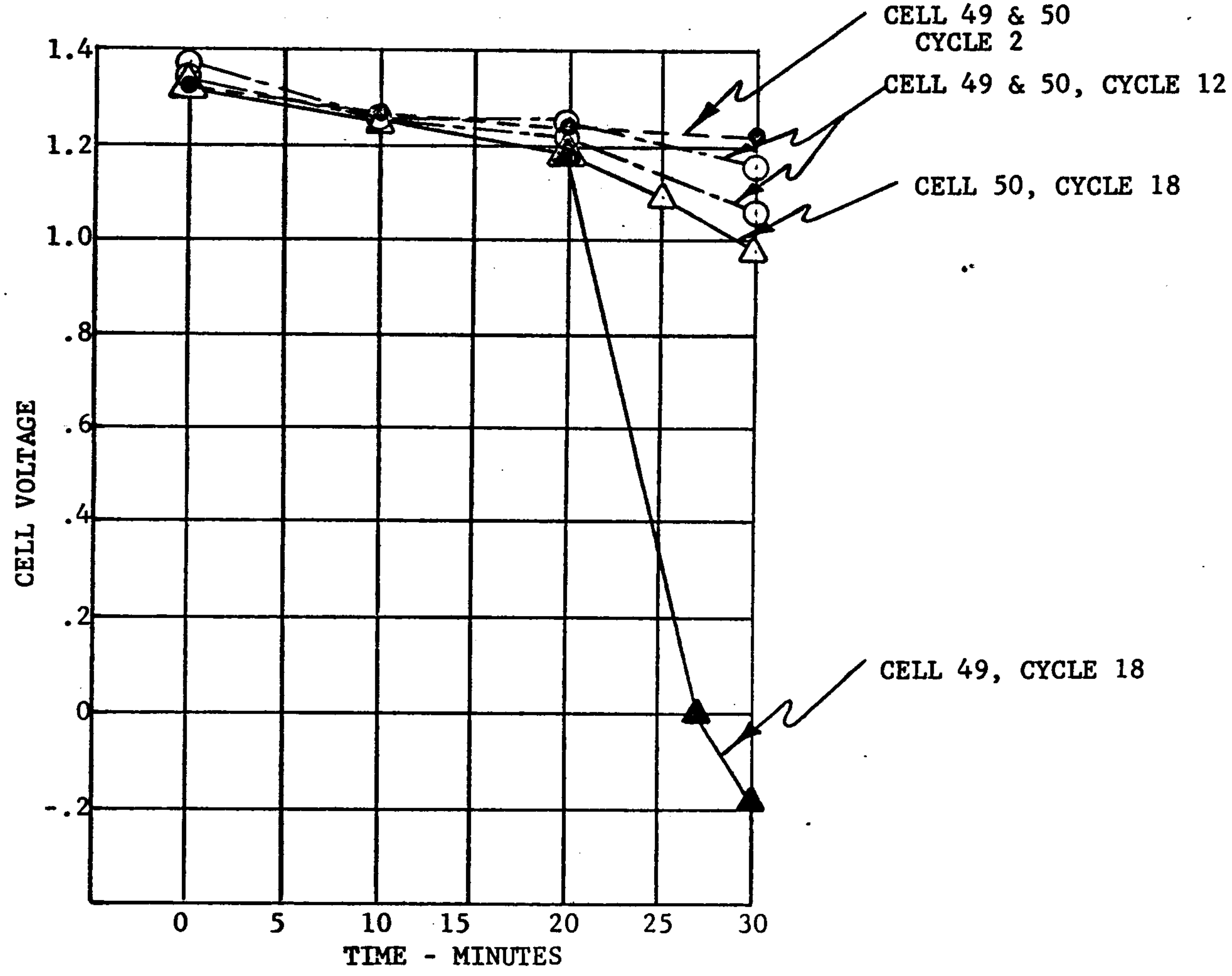

FIGURE 21. CYCLES 2, 12, 18 -- 50% DOD, 95°F

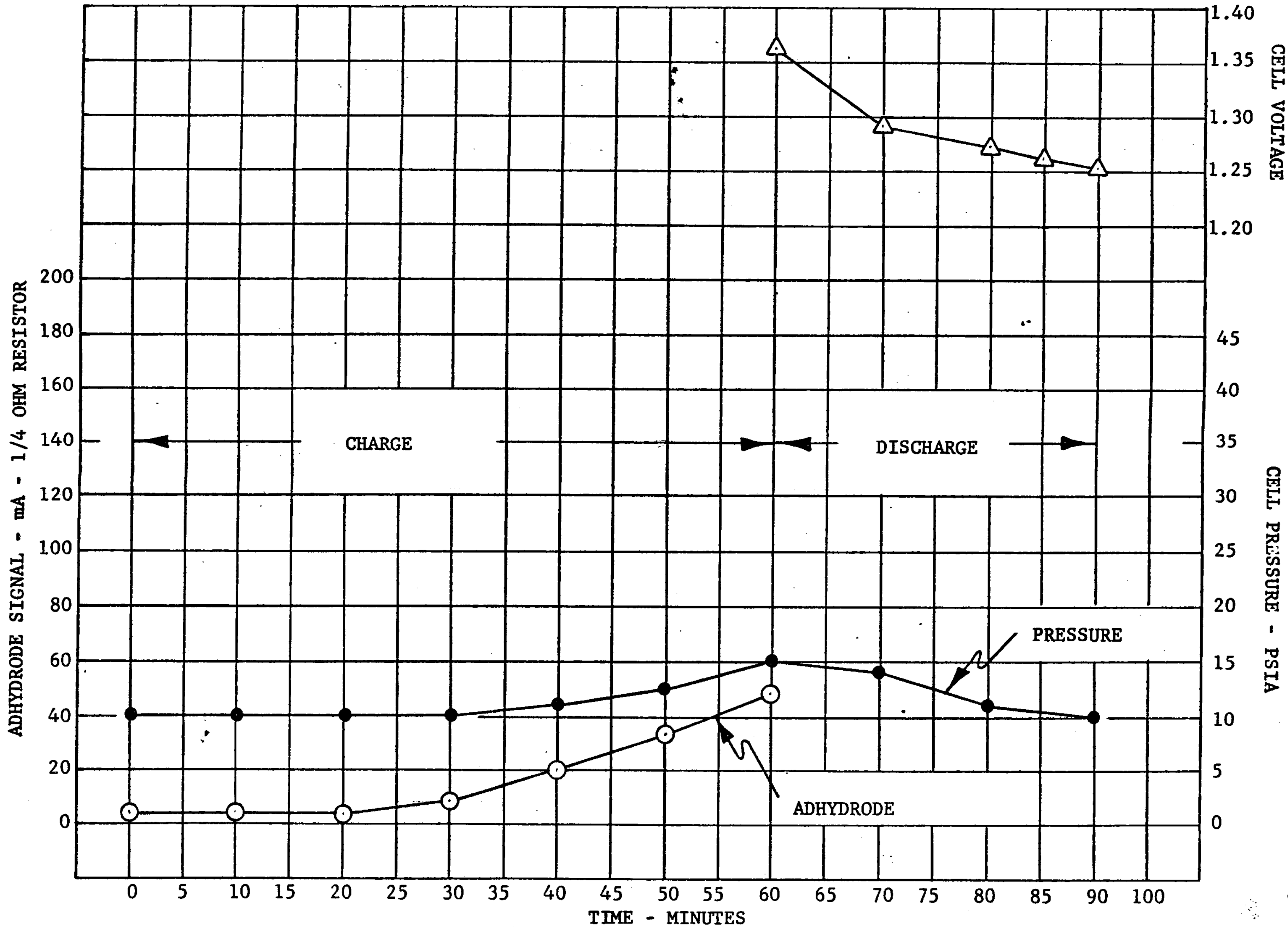

FIGURE 22. ADHYDRODE SIGNAL Vs. PRESSURE & CELL VOLTAGE - CYCLE 3, 10% DOD, 100°F

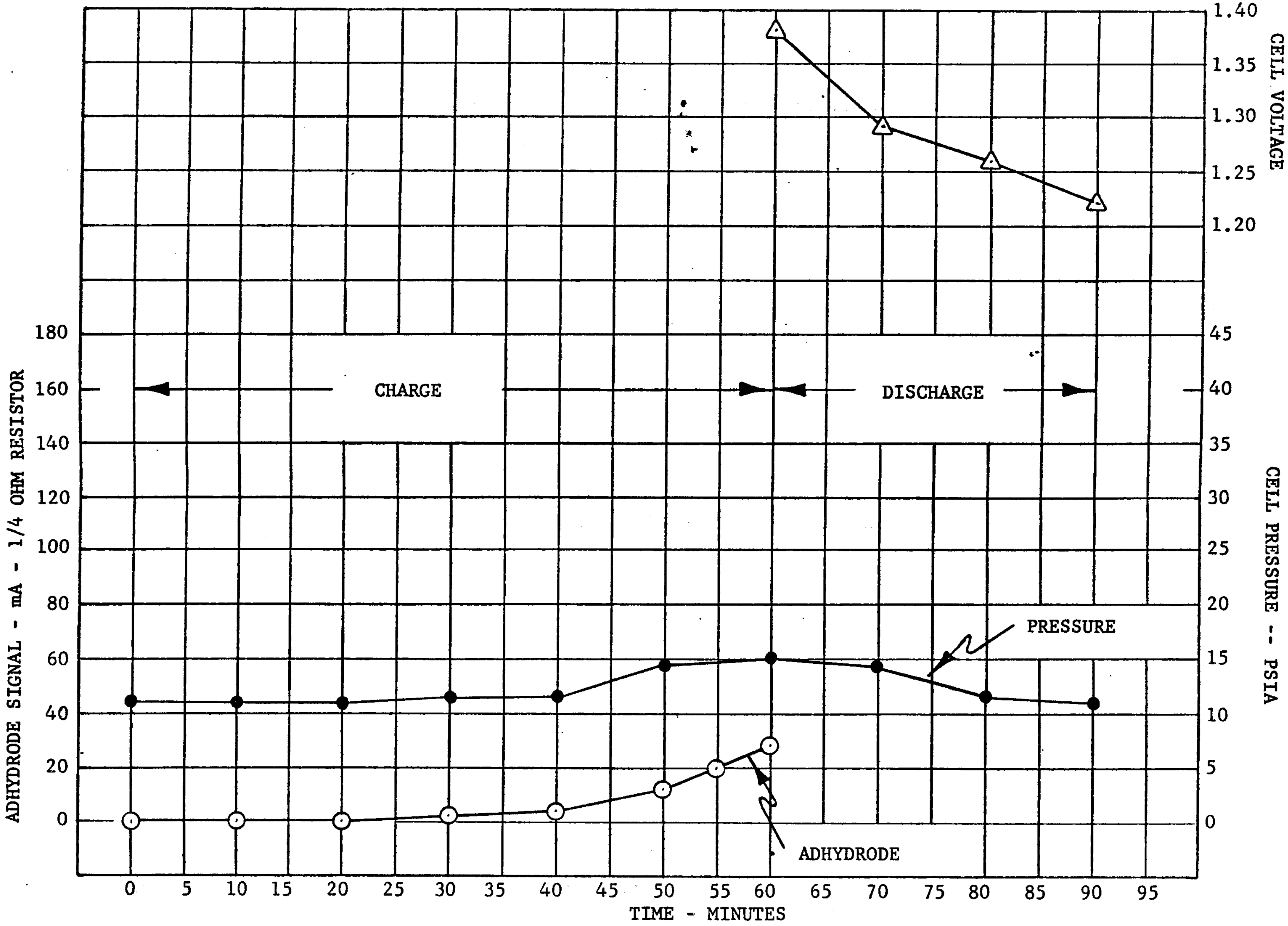

FIGURE 23. ADHYDRODE SIGNAL Vs. PRESSURE & CELL VOLTAGE
CYCLE NO. 142, 10% DOD, 100°F

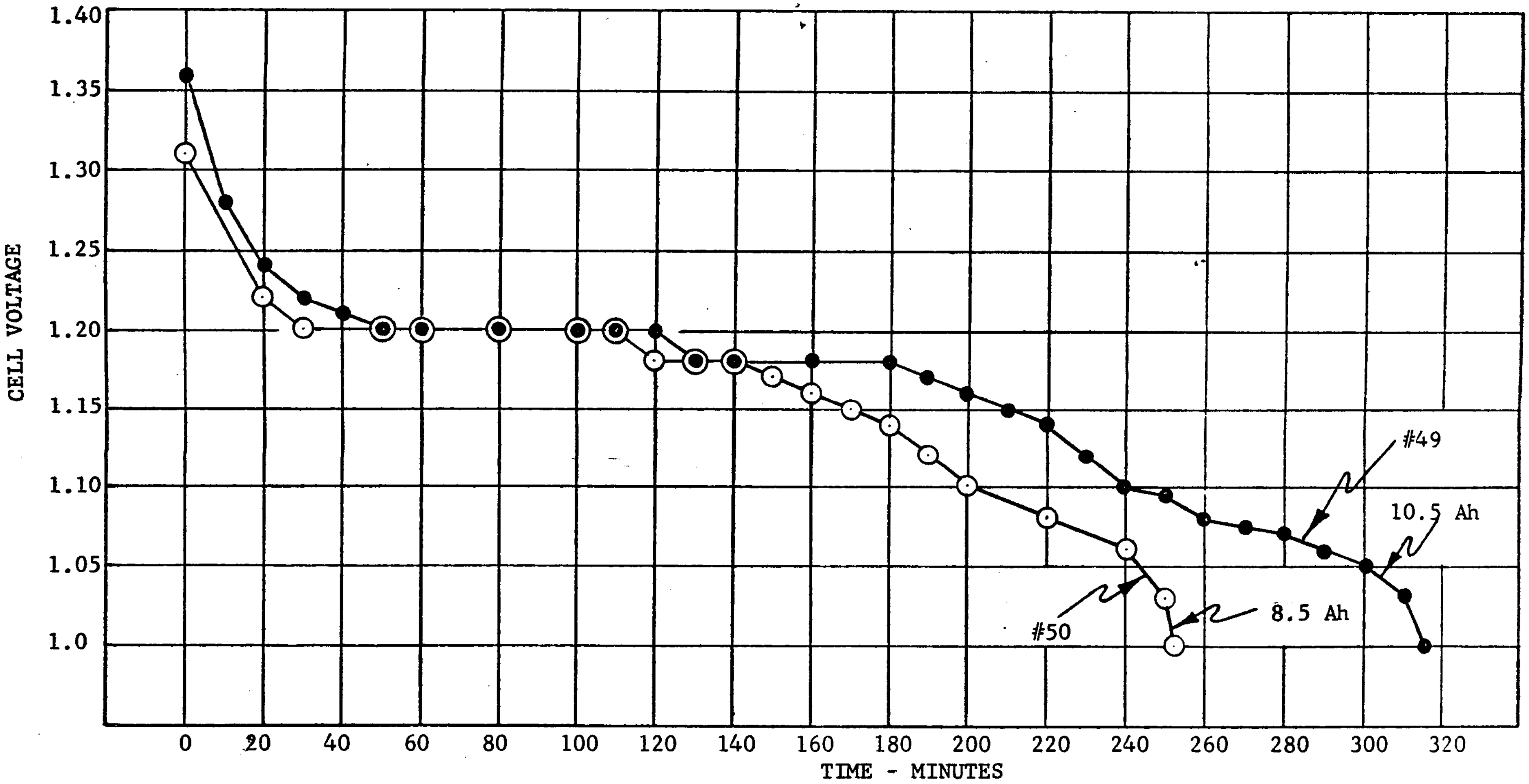

FIGURE 24. RESIDUAL CAPACITY AFTER 158, 10% DOD CYCLES @ 100°F, C/5 DISCHARGE

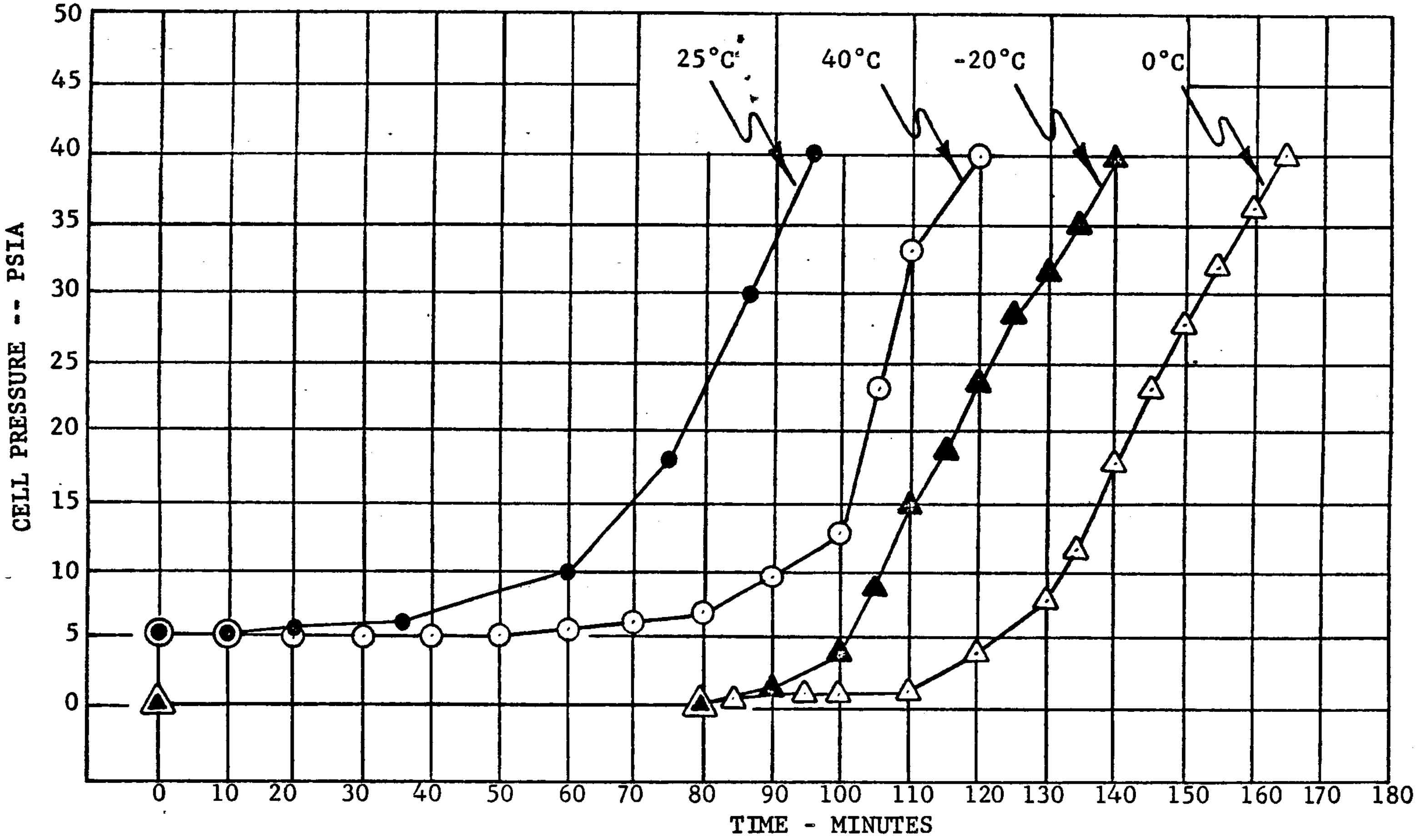

FIGURE 25. C/2 CHARGE TO 40 PSIA -- VO-12HSAD CELLS

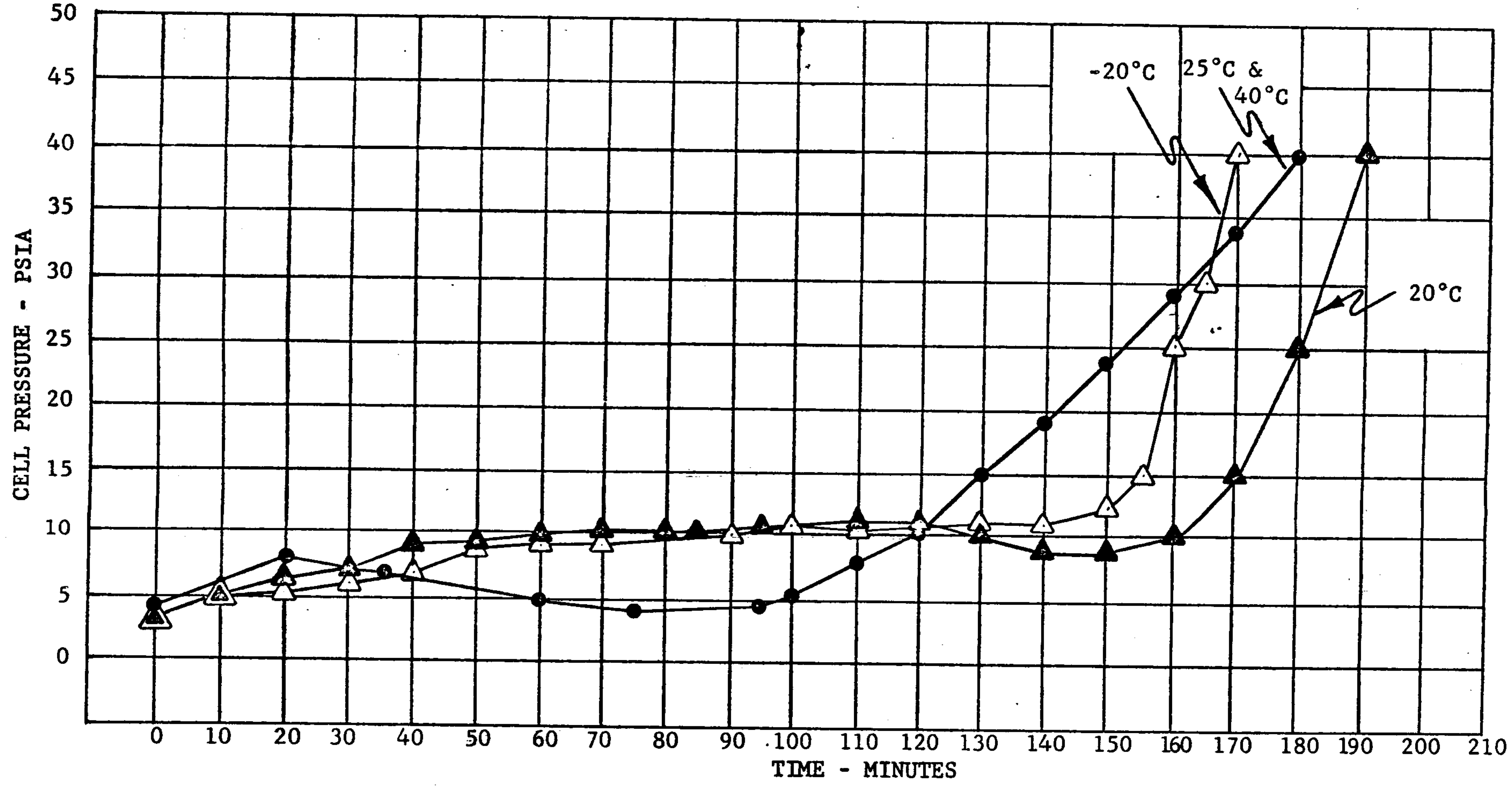

FIGURE 26. C/2 CHARGE TO 40 PSIA - EXPERIMENTAL CELLS WITH FUEL CELL ELECTRODES

CONCLUSIONS

The testing of hermetically sealed nickel-cadmium cells equipped with both a fuel cell scavenger electrode and an active Adhydrode has shown these cells to be superior to conventional (VO-12HSAD) cells equipped with only an active Adhydrode. This superiority is demonstrated by (1) the ability of the cells to be cycled at 60% depth of discharge, (2) the improved low temperature performance, (3) the improved gassing characteristics shown by the ability of the scavenger electrode to keep the cell pressure low independent of the internal cell atmosphere and most important, (4) the rapid decay of the Adhydrode signal upon interruption of charge.

FUTURE WORK

Additional emphasis will be given to high temperature testing (40°C).

The required cells for delivery are in the process of fabrication and should be ready by the required delivery date.

REFERENCES

(1) S. Lerner and H. N. Seiger, First Quarterly Report, "Characterization of Recombination and Control Electrodes for Spacecraft Nickel Cadmium Cells", Contract No. NAS 5-10241, Sept. 9, 1966.

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